Studies of Brisbane municipal water quality using Inductively Coupled Plasma – Mass Spectrometry and Chemometrics

Kate Elizabeth Brough
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Abstract

Water is one of the most basic and essential constituents of the global environment and is an especially precious resource in Australia due to its extremes of drought and flood. The main focus of this study has been the elemental composition of drinking water (including heavy metal content), an integral aspect of water quality. Some elements appear naturally in the environment and are vital to human health; whereas others, such as heavy metals, can result from anthropogenic sources like industry, urban run-off or atmospheric emission. The levels of heavy metals require management and regulation as many are potentially harmful at high concentrations. However, heavy metal and trace element concentrations in drinking water in the South East Queensland region have not been widely studied.

The aim of this research was to analyse a variety of potable water samples from the greater Brisbane area through the combined use of Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) and chemometrics. The capital city of Queensland, Brisbane, is located in the state's south east, and it is this South East Queensland region that was investigated. The overall objective of this research was an exploratory analysis of the water supply system with respect to water sources, source contaminants, and the effects of changing climatic conditions upon the drinking water profile in a large conurbation such as South East Queensland. This has been achieved through a longitudinal study of quantitative water quality data collected via ICP-MS. Historical data were defined as data collected by undergraduate students from 2008 to 2012 as part of a practical exercise. Current data included samples collected in 2013 from Mount Crosby West Bank Water Treatment Plant (WTP), from the raw water sources feeding Mount Crosby West Bank WTP, from the mains water distribution system at various locations and from numerous suburban homes.

More than 400 samples were collected over this six year period and analysed by ICP-MS. Most were tap water samples; tank waters, filtered waters and bottled waters also featured prominently. Raw, mains and treated waters were similarly collected and analysed in 2013. Raw data from all six years has been examined for adherence to the 2011 Australian Drinking Water Guidelines (ADWG). The changes in trace element and heavy metal concentrations between the WTP and the consumers' tap have also been examined.

Almost all elements in all samples were within the 2011 ADWG. Health guidelines were rarely exceeded, and elements that exceeded aesthetic guidelines, such as iron and copper, were attributable to household plumbing systems. Additionally, concentrations of elements increased between the WTP and the mains water distribution system, while concentrations between mains waters and tap waters remained very similar.

Various chemometric techniques were then employed to investigate the distinctions between different water sources. The most distinguishable water sources in comparison to tap water are raw, bottled, mains and tank waters respectively. Filtered waters and tap waters are shown to be very closely related. The nature of water mixing in South East Queensland also meant that tap waters could not be traced back to their raw source water origins.

The changing patterns of metal ions have been studied longitudinally in conjunction with the climatic conditions experienced over this six year period. The results of the PROMETHEE and GAIA analysis do not indicate a preference or detectable change in water quality in relation to climatic conditions.

Partial Least Squares (PLS) analysis used the historical sample data and a selection of the trace element and heavy metal variables to develop a predictive model for water quality, where current samples from 2013 were left out and predicted. Construction of a valid model indicates that such a model may be used as a baseline predictive model for future analyses with a minimised number of variables, culminating in cheaper and faster analyses. The application of four different chemometric techniques maximised the elucidation of information from the water quality data.

Overall, this thesis represents a comprehensive study of Brisbane municipal water quality based on the trace element and heavy metal concentrations of various water sources. The combined use of ICP-MS and several chemometric techniques allowed the fingerprints of various water sources to be distinguished, and the effects of changing climatic conditions on water quality to be identified, as well as for the construction of a valid PLS model, suggesting that metals can be predictors of water quality. This research contributes significantly to the understanding of water quality and supply in Brisbane, Australia, particularly regarding water quality at the consumers' tap, and to knowledge of relationships between a variety of water sources. The chemometric techniques employed here are applicable to water quality investigations worldwide.

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Glossary of Terms

Agricultural	Refers to contamination sources related to the cultivation and production of crops, livestock, or poultry.
Anthropogenic	Refers to trace element and heavy metal contamination caused by humans or human activity.
Carcinogen	Any substance or agent that promotes cancer.
Chemometrics	Consists of a multitude of techniques for multivariate analysis and pattern recognition, supervised and unsupervised.
Diagenesis	The physical and chemical changes occurring in sediments between the times of deposition and solidification (into rocks).
Eigenvalues	A special set of scalar variables associated with a system of linear (or matrix) equations known as the principal components. The sum of the eiganvalues will equal the number of original variables. The larger the eigenvalue, the more important it is and the more information it contains.
Eigenvectors	The set of vectors or principal components extracted from the original variables. Each eigenvector will have an associated eigenvalue.
Error	The disagreement between a measurement and the true or accepted value. Errors may be random or systematic.
Esky©	An Australian brand of portable coolers/iceboxes.
Historical data	Data collected from undergraduate student experiments from 2008 to 2012 that forms the longitudinal study for this research.
Industrial	Refers to sources of contamination originating from industrial manufacturing, productions and industrial wastes.
Isobaric Interference	A type of elemental interference in ICP-MS that is caused by isotopes of different elements which form singly or doubly charged ions of the same nominal mass-to-charge ratio and which cannot be resolved by the mass spectrometer in use.
Lithogenic	Refers to natural sources of trace element and heavy metal contamination, as in from rocks, sediments, minerals, etc.
Microbial	Refers to contamination due to the presence or growth of harmful microorganisms in waters.

Non-parametric	A statistical method wherein the data is not required to fit a normal distribution.
Objects	All water samples, historical and current, collected and analysed in this research.
Physical characteristics	Measurable characteristics that determine largely subjective qualities of water, such as taste, odour, and 'feel': true colour, turbidity, hardness, total dissolved solids (TDS), pH, temperature, taste and odour, dissolved oxygen. Physical characteristics were not measured in this research; however residents were surveyed on appearance, odour and taste of their water.
Raw water	Untreated water sourced directly from dams, lakes or rivers.
Uncertainty	A range around a value such that any repetition of the measurement will produce a new result that lies within this range.
Unsupervised	A pattern recognition method that checks for groupings of different objects using chemical measurements.
Urbanisation	The physical growth of an urban area accompanied by an increasing population.
Variables	Each isotope and tuning step of all 26 trace elements and heavy metals analysed in this research.

Businesses

H_2Flow	H_2Flow is 100% Queensland family owned and operated. Established in 2001, this private family business is a support contractor to the civil and construction industries, horticultural industry, private sector and Government.
Seqwater	Seqwater is one of Australia's largest water businesses with the most geographically spread and diverse asset base of any capital city water authority.

List of Abbreviations

ADWG	Australian Drinking Water Guidelines
Amu	Atomic mass units
ANN	Artificial Neural Networks
ANZECC/ ARMCANZ	Australian and New Zealand Environmental and Conservation Council / Agricultural and Resource Management Council of Australia and New Zealand
CA	Cluster Analysis
CBD	Central Business District
CPS	Counts per second
CRM	Certified Reference Material
DA	Discriminant Analysis
DNRM	Department of Natural Resources and Mines
FA	Factor Analysis
GAIA	Graphical Analysis for Interactive Assistance
GI	Gastrointestinal
HCA	Hierarchical Cluster Analysis
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
ISTD	Internal Standard
K	Kelvin
LGA	Local Government Area
MCDM	Multicriteria Decision Making
MDL	Method Detection Limit
mg	Milligrams (10^{-3} grams)
MHz	Megahertz
ML	Megalitres
mL	Millilitres (10^{-3} litres)

mm	Millimetres (10^{-3} metres)
MΩ	Megaohms
m/z	Mass to charge ratio
ng	Nanograms (10^{-9} grams)
NPI	National Pollutant Inventory
ORS	Octopole Reaction System
PA or P/A	Pulse/Analog
PET	Polyethylene terephthalate
PCA	Principal Component Analysis
PCs	Principal Components
PLS	Partial Least Squares
ppb	Parts per billion (µg/L)
ppm	Parts per million (mg/L)
ppt	Parts per trillion (ng/L)
PROMETHEE	Preference Ranking Organisation METHod for Enrichment Evaluations
QP	Quadrupole
RF	Radio Frequency
RMSEP	Root Mean Square Error of Prediction
SEQ	South East Queensland
TA	Trend Analysis
µg	Micrograms (10^{-6} grams)
µL	Microliters (10^{-6} litres)
US EPA	United States Environmental Protection Agency
WHO	World Health Organisation
WTP	Water Treatment Plant

Statement of Original Authorship

The work contained in this thesis has not been previously submitted to meet requirements for an award at this or any other higher education institution. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made.

QUT Verified Signature

Signature:

Date: December, 2014

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Chapter One: Introduction

The purpose of this research is to investigate the concentration of trace elements and heavy metals in potable water of the greater Brisbane area. The introduction to this thesis contextualises the importance of this research. The aim and objectives of this research are presented, key concepts of water in South East Queensland defined, and the relevant toxicology and techniques employed to investigate such topics described. The background to each concept is explored, followed by statements on the purpose and significance of this research, detailing why this topic warranted analysis. Finally, the thesis outline, including the intentions of the Literature Review, Research Design and Methodology, Results and Discussion, and Conclusion chapters, is presented.

1.1 Background of Key Concepts

This section evaluates the key concepts of water in South East Queensland, trace element and heavy metal toxicology, analytical techniques and advanced statistical analysis to establish the reasons for pursuing this research topic.

1.1.1 Water in South East Queensland

Known around the world as the 'Sunshine State', Queensland is recognised for its dry, mild winters and hot, humid summers. The tropical climate experienced in the state's south east and capital city of Brisbane makes summer the 'wet season' with frequent afternoon storms. Over the years, South East Queensland has suffered several droughts and floods that have made the use of the Brisbane River and the city's water supply prevalent and ongoing issues. Since its settlement in 1824, the provision of an adequate water supply has had perhaps the greatest impact on the Brisbane River and its tributaries (Gregory, 1996).

Maintaining supply of an adequate quantity and quality of potable water to South East Queensland involves consideration of the history of Brisbane's water supply and the consequences of changing climatic conditions. The history of supplying drinking water began with the construction of a temporary earth dam across a creek which ran near the present Brisbane Grammar School and flowed through the site of the Roma Street railway yards to where City Hall presently stands. Similarly, South Brisbane was served by one

small spring and the large Woolloongabba swamp (Gregory, 1996). The region's first permanent dams, Enoggera and Gold Creek, capable of supplying fresh, clean running water were completed in 1866 and 1886 respectively. Construction on the Mt Crosby Pumping Station began in 1889, but floodwaters in 1890 covered the site, so the pumping station was moved and rebuilt 10 feet (3 metres) above the 1890 flood level, only to be flooded again in 1893 (Gregory, 1996).

Once the water mains crossing the damaged Victoria Bridge were reinstated following the flooding in 1893, adequate **supply** of water to the growing population of Brisbane was achieved and predicted to serve the city for the foreseeable future (Gregory, 1996). However, water **quality** could not be guaranteed. Soil from exposed farmlands that swept into the River during the 1893 floods left the water looking and tasting muddy. Consequently, the first long-term plans to filter Brisbane's water supply were established. The first filtration scheme was constructed years later at Enoggera in 1912. The first treatment plant was completed by 1919 at Mt Crosby, situated on the nearby Holt's Hill, and included eight slow sand filters (Mountains to Mangroves, 2014).

When severe drought caused the Brisbane River to actually stop flowing in 1902, more water storage was deemed necessary and a dam on Cabbage Tree Creek was completed in 1916 (Gregory, 1996). The growing number of dams and catchments on the Brisbane River resulted in the flow of water becoming much more regulated, though water supply inadequately matched the accelerated growth of the city. Attempts to solve this problem involved the construction of more reservoirs in suburban Brisbane in the late 1920s, but these barely affected the supply issue. A minor flood in 1931 reinforced the need for flood mitigation, and a change in government in 1932 meant the establishment of the Stanley River Works Board (SRWB) in 1934. Work began in 1935 on Somerset Dam (built on the Stanley River) and continued until 1943 (Gregory, 1996; Seqwater, 2013g). During this time period, the capacity of the Mt Crosby Treatment Plant was enlarged to treat 18,000,000 gallons (over 68,000,000 litres) of water daily, with the addition of three more slow sand filters and twelve rapid filters, and was also extended to include chlorination in 1925 (Gregory, 1996), followed by the addition of ammonia in 1935.

Droughts in 1937, when the River ceased flowing, and yet again in 1940 and 1941 demonstrated the necessity and ability of Somerset Dam and its water storage system to alleviate water shortages (Gregory, 1996). Post war labour shortages meant construction was delayed, and the dam was completed in 1959. Somerset Dam was built across the

Stanley River in a rocky gorge between Mount Somerset and Little Mount Brisbane, and is a few kilometres upstream from the junction with the Brisbane River and upstream from Lake Wivenhoe (Seqwater, 2013g). Key features of Somerset Dam are shown in Figure 6-1 in Appendix A.

South East Queensland's unpredictable climate again resulted in serious droughts in 1951 and 1952 that strained capacity at an already extended Mt Crosby (Gregory, 1996). New reservoirs had been built to aid the water supply, machinery in the pumping house was converted to electricity and the old slow sand filters were replaced. Until the new low-level filters were ready in 1946 and 1947, the slow sand filters on Holts Hill handled all filtering (Gregory, 1996). To alleviate Brisbane's water shortage, the first new dam to be constructed since Somerset Dam in 1943 was the North Pine Dam, which was operational by 1975. Key features of North Pine Dam are presented in Figure 6-2 in Appendix A. The construction of reservoirs and implementation of upgraded machinery and filters highlights the growing realisation that both the quantity and quality of Brisbane's water supply were linked and in need of regular revision in order to keep pace with the expansion of the city.

The Brisbane Water Board had proposed another site at Middle Creek for decades, but in 1971 the State Government recommended a site ten miles (16 kilometres) further downstream at Wivenhoe, a site well suited to the dual purpose of water storage and flood mitigation and where construction would be less expensive (Gregory, 1996). Construction was approved in 1976 in response to the damaging 1974 Brisbane flood. Even prior to its completion, Wivenhoe mitigated another potentially serious flood in 1983. Approximately 200 separate properties were acquired to provide the 33,750 hectares of land required for the dam, which was constructed across the Brisbane River, approximately 80 kilometres from the Brisbane CBD (Seqwater, 2013j). Finished in 1985, Wivenhoe Dam is a multifunctional facility, where its primary task is to supply safe water to Brisbane and surrounding areas, as well as providing flood mitigation (Seqwater, 2013k). Key features of Wivenhoe Dam can be found in Figure 6-3 in Appendix A. Water from the nearby Somerset Dam can be released into Wivenhoe Dam to supplement the natural flow of the Brisbane River (Seqwater, 2013g). Somerset Dam and Wivenhoe Dam are operated in tandem during flood events to maximise the dams' overall flood mitigation capabilities (Seqwater, 2013c). In addition to supplying potable water to South East Queensland, the energy of the moving water from Lake Wivenhoe is harnessed by two Queensland Government owned energy corporations (Seqwater, 2013k).

From 2003, South East Queensland and indeed much of Australia experienced record-breaking drought, justifying water restrictions and the consideration of alternate water sources and treatment plans. Heavy rain in May 2009 meant drought conditions in Brisbane were lifted. Then in 2010, Brisbane experienced its wettest December on record and wettest December since 1859. The North Pine catchment area received rainfall equivalent to a 1 in 200 year event in 2009, and a 1 in 500 year event in 2010 (Seqwater, 2013a). On 11 January 2011, despite the institution of a comprehensive flood mitigation scheme for the Brisbane River area in response to the devastating flood of 1974, the Brisbane River broke its banks with the flood peaking at 4.45m on January 13 (Seqwater, 2013a). Though this flood peak is the sixth highest in the city's history, Somerset, Wivenhoe and North Pine Dams provided clear flood mitigation benefits, minimising the height of the flood by approximately 2 metres, while Seqwater maintained drinking water supplies to South East Queensland's water grid (Seqwater, 2013d).

The history of Brisbane's water supply and the consequences of changing climatic conditions must be considered in order to maintain supply of an adequate quantity and quality of potable water to South East Queensland. Consequently, site selection for all past and future dams constructed in South East Queensland remains strategic, where such sites are chosen for proximity to catchment areas and at minimal risk of suffering the effects of drought or flood. Catchment areas are described as:

> "an area of land surrounded by natural high features, such as hills or mountains. All the rain that falls onto the catchment flows down hill, as runoff, to a low point like a stream or river. The runoff will eventually flow into a lake or reservoir, dam or out to the ocean. A small amount of the runoff soaks into the soil to replenish groundwater supplies, known as aquifers". (Seqwater, 2013i)

Figure 1-1 specifies the drinking water catchment supply areas in South East Queensland (colour coded) in addition to Local Government Area (LGA) boundaries.

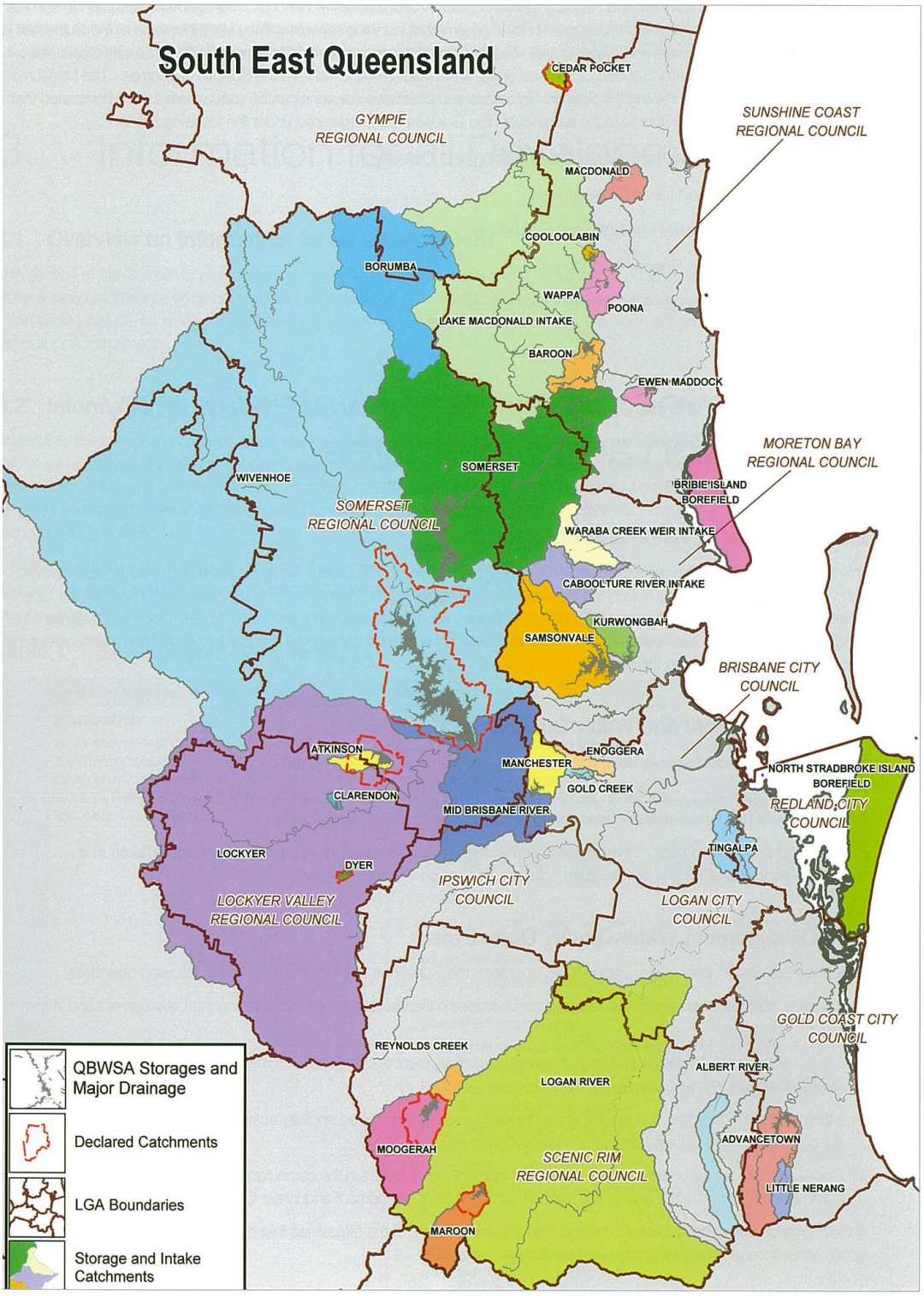


Figure 1-1. Map of South East Queensland specifying drinking water supply catchment areas and Local Government Area Boundaries (legend inset) (Seqwater, 2010). Reprinted from Seqwater Development Guidelines: Development Guidelines for Water Quality Management in Drinking Water Catchments, p. 7, Copyright (2010), with permission from Seqwater.

Water collected from the catchment and stored in dams is treated and passed on to a number of retail entities, like Seqwater, Queensland Urban Utilities and the local government, who are responsible for the supply of treated water to homes in South East Queensland. The Mt Crosby West Bank Water Treatment Plant (WTP) is the main source of treated water for consumers in the greater Brisbane area, and the typical treatment process includes coagulation, flocculation, sedimentation, Dissolved Air Filtration (DAF), chemical disinfection and pH correction. This treatment process is detailed in the following section.

1.1.1.1 Typical Water Treatment Processes

Rain that falls on the Upper Brisbane River catchment (the main catchment servicing Mt Crosby WTP) flows over an extensive area and collects in Wivenhoe Dam. The condition of catchment water is variable, as runoff may carry dirt, contaminants such as chemicals and nutrients, debris and microorganisms into the creeks and rivers that flow into Lake Wivenhoe, some of which are harmful, particularly to humans. When required, the stored water is released downstream into the Brisbane River, where it makes its way to the Mt Crosby Weir and is then pumped up to the West Bank WTP, where it is made safe for drinking (Seqwater, 2013i).

The conventional treatment process used by the majority of Seqwater's treatment plants is, in order: coagulation, flocculation, sedimentation and filtration. Chemicals added to the water at various stages enable the processes to effectively remove potentially harmful contaminants in the raw water to be treated (Seqwater, 2013h). Coagulation is important for treating the highly turbid waters that are frequently collected from the Mt Crosby Weir (Seqwater, 2013i). To lower pH, aluminium sulfate ("alum" or $Al_2(SO_4)_3$) is added to raw water which is then stirred in flash mixers for 20 to 30 seconds, forcing suspended particles to coagulate, a process that can be described as similar to curdling. Flocculation is the clumping of the coagulated suspended particles to form even heavier particles, referred to as "floc". In addition to alum, caustic soda (sodium hydroxide) and slaked lime may also be added to adjust pH, as pH must be in the correct range of pH 6.8 – 7.2 to promote coagulation and flocculation.

Next, the water and floc flow into large sedimentation tanks with a capacity of 6.5 ML. The water settles and the heavy floc particles sink to the bottom, forming a sludge, regularly removed via vacuum (Seqwater, 2013i). The water is then moved to filtration chambers

where a pressurised stream of water saturated with air is injected into it. This process is known as Dissolved Air Filtration (DAF). As masses of very fine oxygen bubbles rise up through the water, any floc particles that did not sink in the sedimentation tanks attach to these bubbles and float to the surface (Seqwater, 2013i). The accumulating floating sludge blanket is removed at regular intervals, and that which remains is clarified water. This clarified water is filtered again through rapid gravity sand filter beds consisting of finely graded silica sand and pebble layers, removing any persisting floc (Seqwater, 2013i).

Visually, at this stage of the treatment process, the water appears ready to drink. However, chemical disinfection and pH correction must be implemented. Chlorine is added as a disinfectant to kill microorganisms, bacteria and any viruses that may be present in the water, while lime is added to correct the pH so as to ensure the water is not too acidic for human consumption, and also so it does not corrode pipes in the distribution networks and homes. Since 2008, fluoride has also been added as a protective dental measure, an initiative of the Queensland Government known as Water Fluoridation Regulation (Seqwater, 2013i). As the treated water leaves the WTP and is pumped to reservoirs, chloramine is added to ensure that any harmful microorganisms are destroyed and do not regrow in the pipes. Chloramine (NH_2Cl) is added because chlorine is only active as a disinfectant for six to eight hours, although local councils often add chlorine to maintain disinfection as the water travels to residences.

The intricate way in which treated water travels to properties around South East Queensland is referred to as the Water Grid and incorporates the complete supply chain from catchment to tap.

1.1.1.2 South East Queensland (SEQ) Water Grid

Seqwater was formed on January 1, 2013 through a merger of three state-owned water businesses, the SEQ Water Grid Manager, LinkWater and the former Seqwater. Seqwater is one of Australia's largest water businesses that brings together diversified water supplies, distribution methods and water industry organisations to expand and interconnect new and existing water sources across the region (Seqwater, 2009, 2013b).

Both Somerset Dam (Lake Somerset) and Wivenhoe, South East Queensland's largest Dam, are part of the SEQ Water Grid, a series of connected dams and water treatment plants, capable of moving potable water around South East Queensland (Seqwater, 2013g). Water from Wivenhoe is treated at both the West Bank and East Bank WTP at Mt Crosby.

Integration of this water with Brisbane's three other major dams (Somerset, Hinze and North Pine) means that not only Brisbane's but all of South East Queensland's water demand will be met into the future (Seqwater, 2013k).

Overall, Seqwater owns and operates 26 dams, 47 weirs, 14 bores and aquifers, and 18 reservoirs, as well as 46 water treatment plants, 3 advanced water treatment plants and the desalination plant on the Gold Coast. Table 1-1 displays all dams and their completion date, while Figure 1-2 and Figure 1-3 show the location of all water treatment plants and reservoirs in South East Queensland.

Table 1-1. Dams owned and operated by Seqwater and their corresponding completion date. Dams highlighted in green are the 12 keys dams across the region that contribute to the water supply system.

Dam	Year Completed
Enoggera	1866
Gold Creek	1885
Poona	1959
Lake Manchester / Cabbage Tree Creek	Constructed - 1916; upgraded - 2008
Somerset	1959
Little Nerang	1961
Moogerah	1961
Wappa	1963
Six Mile Creek Dam / Lake Macdonald	1965
Nindooinbah	1961, upgraded - 1969
Sideling Creek Dam / Lake Kurwongbah	1969
Atkinson	1970
Maroon	1974
North Pine	1976
Cooloolabin	1979
Ewan Maddock	1982
Cedar Pocket	1984
Leslie Harrison Dam / Tingalpa Reservoir	1984
Wivenhoe	1984
Bill Gunn	1987
Baroon Pocket	1989
Hinze	Constructed - 1976; Raised - 1989; Finalised - 2011
Clarendon	1992
Borumba	Stage 1 - 1963; Stage 2 - 1997
Bromelton	2008
Wyaralong	2010

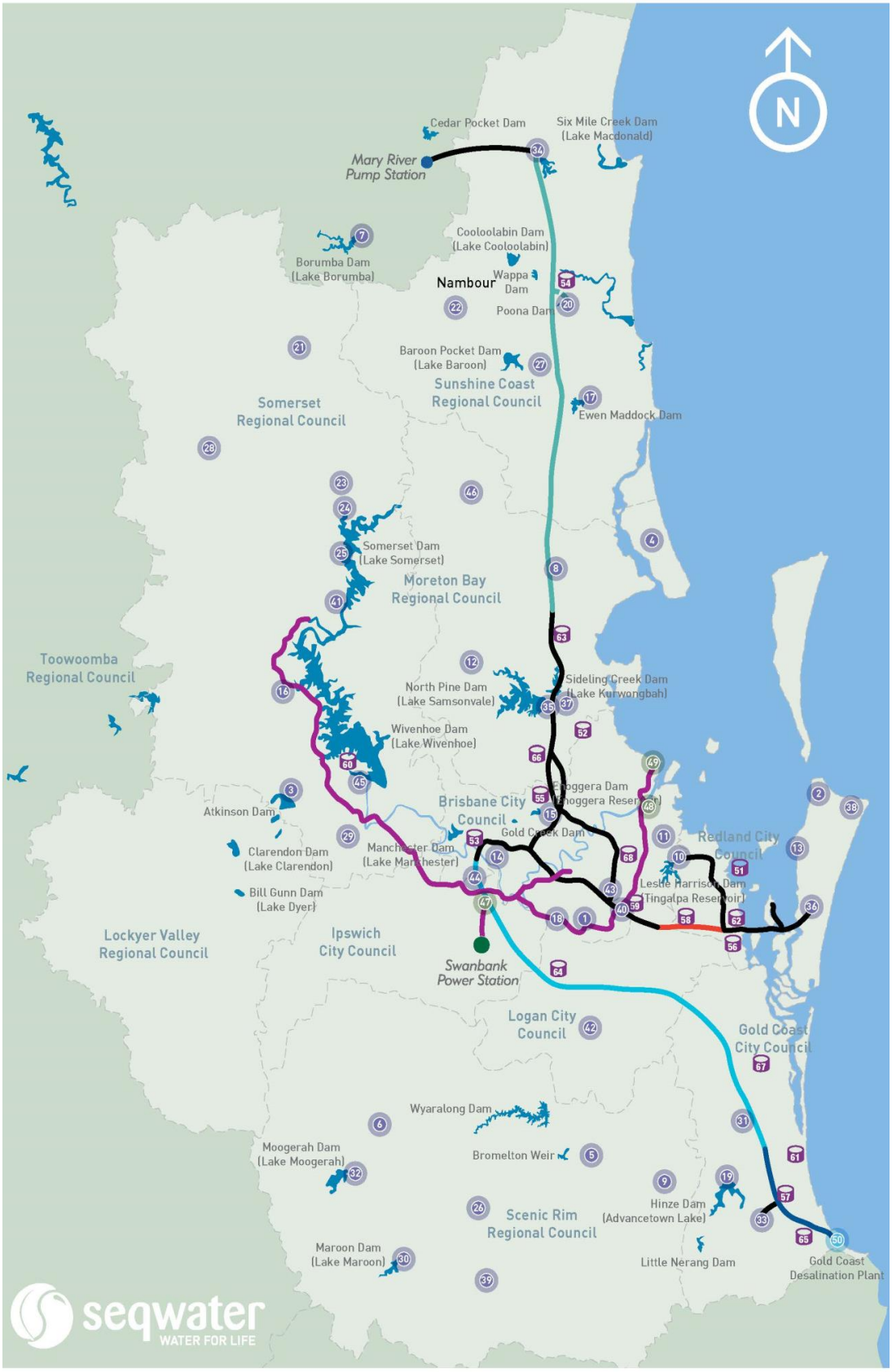


Figure 1-2. Locations of all water treatment plants and reservoirs owned and operated by Seqwater. Figure 1-3 is the corresponding legend for these assets (Seqwater, 2013e). Reprinted from Seqwater - Water Supply, Copyright (2013), with permission from Seqwater.

Figure 1-3. Seqwater assets corresponding to the map shown in Figure 1-2 (Seqwater, 2013e). Reprinted from Seqwater - Water Supply, Copyright (2013), with permission from Seqwater.

The Water Grid allows Seqwater, affiliated corporations and local governments to supply residents of the greater Brisbane area with an adequate quantity of water regardless of changing climatic conditions. However, the quality of potable water is also of utmost importance, where regular monitoring is employed by all organisations to assess the effect of any contaminants on human health, as well as the aesthetic nature of the water. All drinking water consumed in South East Queensland and indeed Australia is produced to be compliant with the Australian Drinking Water Guidelines (ADWG).

1.1.2 Toxicology – Trace Elements and Heavy Metals

There are many constituents of water that are essential for human health, and there are many that are not. The treatment processes applied to raw water are highly efficient at removing the harmful constituents, though 100% removal is unrealistic. As described in section 1.1.1, water transported to treatment plants from dams is runoff from catchment areas that eventually flows into the lake or dam, and as highlighted in Figure 1-1, catchment areas can encompass all types of land and land uses. Urban, agricultural and industrial applications influence runoff quality entering dams and catchments. For example, urban runoff from households, roads and construction sites; animal waste, fertiliser and pesticides from agriculture; and various effluents from industrial activity, all contribute to raw water quality. Catchment areas, lakes and dams must also be considered for natural contributions, based on the geological properties of these areas. Therefore, contaminants can be generally classified as natural, agricultural, industrial, microbial and anthropogenic.

The focus of this research is to investigate the presence of trace elements and heavy metals in water, specifically in drinking water, supplied to the greater Brisbane area. As such, microbial contaminants were not considered sources of trace element and heavy metal contamination, however, they remain important to note as potentially harmful contaminants when discussing water quality. The role of trace elements and heavy metals in water is part of a complex interactive system that occurs throughout the water supply network. Any sudden changes in the concentrations of metals would therefore be reflective of wider changes affecting this whole system. Subsequently, natural (or lithogenic), agricultural, industrial and anthropogenic sources of trace elements and heavy metals were all thoroughly investigated for their contributions to potable water in South East Queensland.

Contamination of the environment and human exposure to metallic elements may occur naturally, for example, by erosion of surface deposits of metal minerals, as well as from human activities, such as mining, smelting, fossil fuel combustion, and industrial application of metals (Nordberg et al., 2007). Many trace elements and heavy metals are naturally occurring in water and positively contribute to human health; in contrast, some are detrimental. Because water is consumed by every human being, it is an obvious source of trace elements and heavy metals entering the body, making the monitoring of drinking

water quality vital. The wider community and water supply industry are instructed as to what constitutes good quality drinking water by the 2011 Australian Drinking Water Guidelines (ADWG), developed by the National Health and Medical Research Council in collaboration with the Natural Resource Management Ministerial Council (National Health and Medical Research Council, 2011). The ADWG are constantly undergoing a revision process that ensures the latest scientific evidence on good quality drinking water is represented. These guidelines are also approved by the World Health Organisation (WHO). The specific section of the 2011 ADWG of interest for this research is Chapter 10: Monitoring Specific Characteristics in Drinking Water. Table 1-2 is a condensed version of Table 10.5 of the Guidelines, which contains the values relevant for this research.

Table 1-2. Guideline values of trace elements and heavy metals of interest, taken from *Table 10.5 - Guideline values for physical and chemical characteristics* in the 2011 ADWG. c denotes "Insufficient data to set a guideline value based on health considerations" (National Health and Medical Research Council, 2011).

Characteristic	Guideline values (mg/L)		Comments
	Health	Aesthetic	
Aluminium (acid-soluble)	c	0.2	Guideline value based on post-flocculation problems; <0.1 mg/L desirable. Lower levels needed for renal dialysis. No health based guideline value can be established currently.
Antimony	0.003		Exposure may rise with increasing use of antimony-tin solder.
Arsenic	0.01		From natural sources and mining/industrial/agricultural wastes.
Barium	2		Primarily from natural sources.
Beryllium	0.06		From weathering rocks, atmospheric deposition (burning fossil fuels) discharges.
Cadmium	0.002		Indicates industrial or agricultural contamination; from impurities in galvanised (zinc) fittings, solders and brasses.
Chromium (as Cr(VI))	0.05		From industrial/agricultural contamination of raw water or corrosion of materials in distribution system/plumbing. If guideline value exceeded, analyse for hexavalent chromium.
Copper	2	1	From corrosion of pipes/fittings by salt, low pH water. Taste threshold 3 mg/L. High concentrations colour water blue/green. >1 mg/L may stain fittings. >2 mg/L can cause ill effects in some people.
Iron	c	0.3	Occurs naturally in water, usually at <1 mg/L, but up to 100 mg/L in oxygen-depleted groundwater. Taste threshold 0.3 mg/L. High concentrations stain laundry and fittings. Iron bacteria cause blockages, taste/odour, and corrosion.
Lead	0.01		Occurs in water via dissolution from natural sources or household plumbing containing lead (e.g. pipes, solders).
Manganese	0.5	0.1	Occurs naturally in water; low in surface water, higher in oxygen-depleted water (e.g. groundwater at bottom of deep storages). >0.1 mg/L causes taste, staining. <0.05 mg/L desirable.
Mercury	0.001		From industrial emissions/spills. Very low concentrations occur naturally. Organic forms most toxic, but these are associated with biota, not water.
Molybdenum	0.05		Concentrations usually <0.01 mg/L; higher concentrations from mining, agriculture or fly-ash deposits from coal-fuelled power stations.
Nickel	0.02		Concentrations usually very low; but up to 0.5 mg/L reported after prolonged contact of water with nickel-plated fittings.
Selenium	0.01		Generally very low concentrations in natural water.
Silver	0.1		Concentrations generally very low. Silver and silver salts occasionally used for disinfection.
Sodium	Not necessary	180	Natural component of water. Guideline value is taste threshold.
Uranium	0.017		Occurs naturally, or from release of mill tailings, combustion of coal and phosphate fertilisers.
Zinc	c	3	Usually from corrosion of galvanised pipes/fittings and brasses. Natural concentrations generally <0.01 mg/L. Taste problems >3 mg/L.

Additional metals of interest in this research that are not listed in Table 1-2 are, most notably, the essential trace elements magnesium, potassium and calcium. This is believed to be because, as for sodium, a health guideline is not necessary as these elements are natural components of water and are required for many functions within a healthy body. Similarly, cobalt, a metal found in vitamin B-12, does not warrant a guideline because it is naturally occurring and excess is rare. Thallium and thorium are partially soluble and insoluble in water, respectively, and while abundant in nature, are uncommon in industry and therefore are not considered a concern in drinking water. Finally, vanadium is never found unbound in nature (Lenntech BV, 2012), and despite its solubility in water and occasional use in industry, is not considered a hazard.

In addition to the aesthetic guidelines included for the enjoyment of water, the ADWG more importantly provide guideline values for health, as there are many ways in which these trace elements and heavy metals may affect the human body. Metals do not break down. Consequently, a metal stays in the body until it is excreted. During this time, the metals may be transformed into other more toxic or less toxic species (Nordberg et al., 2007).

Table 1-3 separates trace elements and heavy metals that have positive effects on human health from those that are damaging, as well as highlighting the concentrations required. A trace element or heavy metal is essential if a deficiency impairs a biochemical or functional process and replacement of the element corrects this impairment (Toffaletti, 2005).

Table 1-3: Essential and non-essential trace elements and heavy metals required by the body and the appropriate concentrations of each (Toffaletti, 2005).

	Proven Essential	Probably Essential	Non-essential
Trace (mg/L)	Fe, Zn, Cu		
Ultratrace (µg/L)	Mn, Co, Se, Mo, Cr, I	Ni, V, Sb	Al, As, Cd, F, Au, Pb, Hg, Si

Although many trace elements and heavy metals are essential, an excess of any can be harmful. Parts of the body adversely affected by trace elements and heavy metals are detailed in Table 1-4. In addition to specific organs, these elements target the alimentary system, which includes the body structures involved in preparing food for absorption into the body and the excretion of waste products, as well as the hematopoietic system, which includes the blood-producing organs, principally the bone marrow, spleen and lymph nodes.

Table 1-4. Organs and systems targeted by different trace elements and heavy metals (Gaw et al., 1999; Glanze, 1996; Toffaletti, 2005).

Metal	Uptake Form	Target Organs									
		Liver	Kidneys	Lungs	Alimentary system	GI Tract	Heart	Bones	Testes	Hematopoietic system	Brain
Arsenic	As(III) and As(V)	X	X	X	X						
Antimony		X	X								X
Bismuth		X	X								
Cadmium	$CdCl_2$, CdO	X	X			X	X	X	X	X	
Chromium	Cr(III) and Cr(VI)	X				X					
Copper	Inorganic salts					X					
Iron	Inorganic salts	X					X				
Lead	Inorganic salts		X		X			X			X
Manganese		X	X								X
Mercury	Chloride and organic compounds	X	X								X
Nickel	Inorganic salts	X	X	X							X
Selenium	Se(IV), Se(VI) and organoselenium forms	X		X		X					X
Uranium	Inorganic salts	X	X				X				X
Vanadium	Inorganic salts	X		X							
Zinc	Inorganic salts					X					

Two major factors that influence toxicology are the route of exposure, and the duration and frequency of exposure (Casarett et al., 2007). The major pathways by which toxic agents gain access to the body are via the gastrointestinal (GI) tract (ingestion), lungs (inhalation), and skin penetration (topical, percutaneous, or dermal). Duration and frequency of exposure can be broadly classified into acute and chronic exposure. Acute exposure is defined as exposure to a chemical for less than 24 hours. While acute exposure usually refers to a single administration or incident, repeated exposures may be given within a 24 hour period for some slightly toxic or practically non-toxic chemicals (Casarett et al., 2007). Repeated exposure for more than three months, usually occurring

for many months and years, is known as chronic exposure. Long-term repeated exposure can occur by any route, but most often occurs by the oral route, where the chemical is added directly to the diet (Casarett et al., 2007). The toxic effects of many elements and compounds are quite different following acute exposure from those produced by chronic exposure. Chronic exposure may also produce some immediate acute effects after each administration, in addition to the long-term chronic effects of the element (Casarett et al., 2007).

Ingestion of metals via food and drinking water is ordinarily the main pathway of exposure for the general population (Nordberg et al., 2007). Drinking water is considered a significant route of exposure for arsenic, aluminium, iron, uranium, and sometimes manganese, cadmium and lead. Many elements have acute toxicities, where effects become apparent within hours, but can be reversed when treated properly. Metals like arsenic and mercury have chronic toxicities, where effects remain unnoticed for extended periods of time, and these metals can bioaccumulate in one or several vital organs, commonly the liver and/or the kidneys, with excretion rates or biological half-times varying from days to months (Nordberg et al., 2007).

The fine line between essential and harmful concentrations of trace elements and heavy metals that may be consumed in drinking water reinforces the fact that the determination of contaminants in water supplied to the greater Brisbane area is a prevalent point of research. There are numerous tools available to competently perform environmental analyses, but the determination of the elements of interest in this research was accomplished by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS).

1.1.3 Environmental Analysis

There is a wide variety of chromatographic and spectroscopic techniques used in analytical chemistry. Environmental samples, including water, are commonly analysed using atomic spectroscopy methods. Atomic spectroscopy has become established due to its ability to provide very sensitive, accurate, precise determinations of trace and ultratrace elements and species in liquid samples, such as high-purity solutions, environmental materials, and different types of waters (rain, tap, river, sea or waste) (Becker, 2005).

Atomic spectroscopy encompasses Graphite Furnace Atomic Absorption Spectrometry (GFAAS), Flame Atomic Absorption Spectrometry (FAAS), Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). ICP-MS is considered the best choice because of its rapid, multi-element capabilities like ICP-OES, combined with superb detection limits like GFAAS (Thomas, 2001-2002), dynamic range, and high sample throughput.

Advances in laser ablation sample introduction systems mean that ICP-MS instrumentation is now available for use on any sample matrix. A major advantage of ICP-MS analysis is the ability of the instrumentation to handle complex sample matrices. As in this research, no additional sample pre-treatment is required for the complex sample matrix of water outside of acidification and refrigeration for preservation. The multi-element capability of ICP-MS describes its ability to distinguish one element from another in a complex sample and the ability to perform simultaneous multi-element analyses with high sensitivity, low detection limits, and isotope measurement capabilities, all while maintaining a high sample throughput, where many samples can be easily and automatically analysed in a timely manner (Cizdziel, 2010).

Several distinct parts constitute an ICP-MS instrument, including the sample introduction system, ion generation in the inductively coupled plasma, the plasma/vacuum interface, the collision/reaction cell, ion focusing lenses, and ion separation and measurement. The ICP-MS instrument used in this research, pictured in Figure 1-4, was the Agilent 7500ce ICP-MS with an Octopole Reaction System (ORS). A brief overview of each section of this instrument will highlight the advantages of this technique.

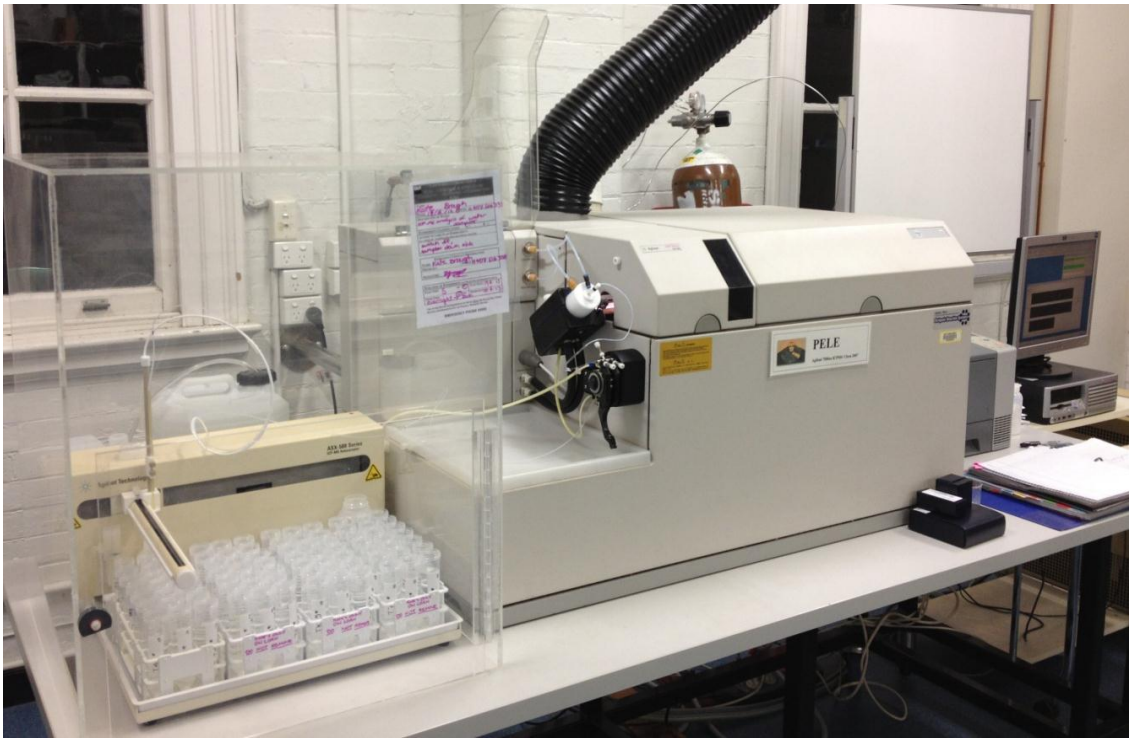


Figure 1-4. The Agilent 7500ce ICP-MS with ORS instrument used for this research at QUT Gardens Point.

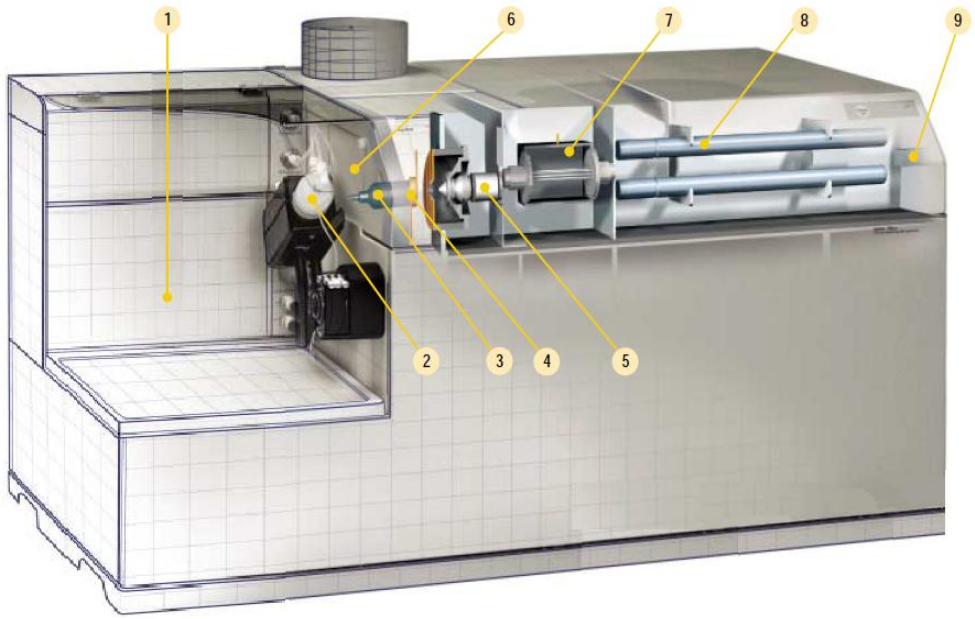


Figure 1-5. Schematic diagram of the Agilent 7500ce ICP-MS with ORS instrument pictured in Figure 1-4 (Agilent Technologies Inc., 2004a). **Reprinted from Agilent 7500 Series ICP-MS, pp. 6-7, Copyright (2004), with permission from Agilent Technologies Inc.**

As shown in Figure 1-5, the numbers displayed on the schematic of the Agilent 7500ce ICP-MS with ORS instrument correspond to a section or function of this particular instrument. Number one indicates the open sample introduction area. Next to this, number two is the Peltier temperature controlled spray chamber that reduces oxide formation and changes in laboratory temperature. The spray chamber uses a nebuliser to aerosolise the liquid sample, removing the larger aerosol droplets before moving the sample into the path of the argon plasma. At number three, the high temperature (10,000 K) argon plasma, contained in a quartz tube and ignited by a 27.12 MHz radio frequency, serves to rapidly dry, decompose, vaporise, atomise and ionise each atom (Agilent Technologies Inc., 2005b).

The Agilent Shield Torch System (STS), number four in Figure 1-5, controls ion energies for increased sensitivity and improved interference removal in ORS collision mode, using energy discrimination (Agilent Technologies Inc., 2004a). Number five, the plasma/vacuum interface, is located approximately 7 mm from the end of a load coil, where the highest level of ions is present. Here, the positively charged ions produced in the plasma are extracted into the vacuum system through very small (1 mm) orifices in a pair of interface cones. The small orifices are used to maintain high vacuum in the mass spectrometer region (Agilent Technologies Inc., 2005b). To minimise background noise, the Agilent 7500ce instrument used in this research uses a high-transmission, off-axis lens arrangement to separate the positively charged ions from the photons and neutral particles. The Active Mass Flow Control (AMFC), number six, is designed by Agilent to precisely control all standard gas flows with sophisticated electronic pressure sensors (Agilent Technologies Inc., 2004a).

Similarly, an Octopole Reaction System (ORS) is featured in order to minimise interferences. Area number seven on Figure 1-5 shows the collision/reaction cell that facilitates the highly efficient removal of polyatomic interferences using two modes: helium (He) collision mode and hydrogen (H_2) reaction mode (Agilent Technologies Inc., 2004a). Then the quadrupole mass spectrometer, number eight on the schematic diagram, uses a combination of DC (direct current) and AC (alternating current) electrical fields and hyperbolic cross section rods to separate ions based on their mass to charge ratio (m/z) (Agilent Technologies Inc., 2005b). Finally, the electron multiplier, number nine, detects each ion as it exits the quadrupole. The simultaneous pulse/analog detector in the ICP-MS instrument is largely responsible for the characteristics of very high sensitivity and low

random background noise, for which the technique is well known (Agilent Technologies Inc., 2005b). The magnitude of the electrical pulses detected corresponds to the number of analyte ions present in the sample, where nine orders of dynamic range (with a maximum of >1000 parts per million) are measurable by instruments with the ORS system (Agilent Technologies Inc., 2004a).

The generation, transportation, and detection of significant numbers of positively charged ions, as described above, gives ICP-MS its characteristic for ultratrace detection capabilities. The Agilent 7500ce instrument used in this research has typical detection capabilities as low as 0.1 parts per billion (ppb or µg/L), equivalent to 1 part per trillion (ppt or ng/L), up to thousands of parts per million (ppm or mg/L). The general process of sample analysis (excluding a collision/reaction cell) is represented in Figure 1-6.

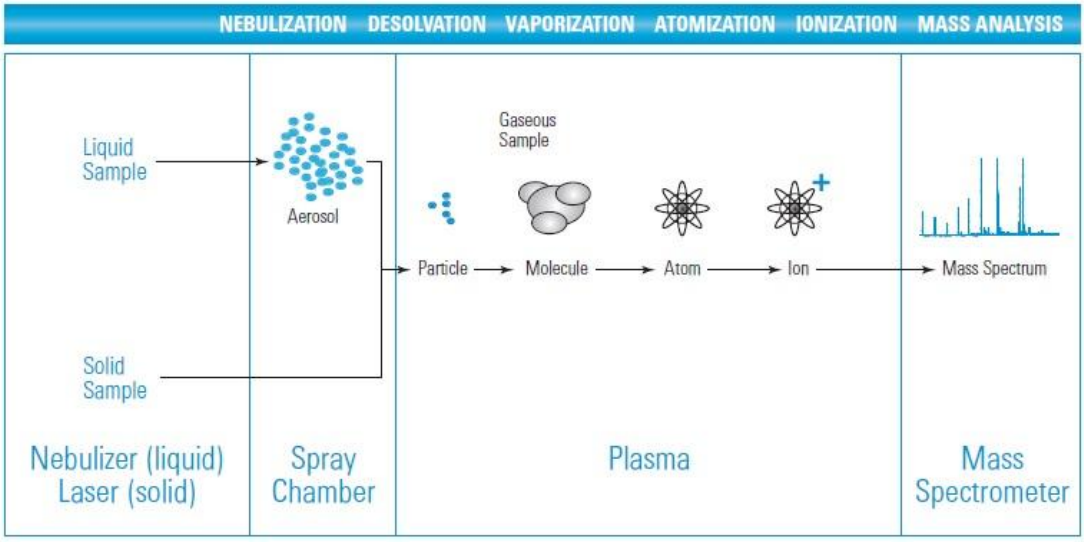


Figure 1-6. Schematic representation of the sample analysis process via ICP-MS (excluding a collision/reaction cell, positioned before the mass spectrometer in selected Agilent models) (Agilent Technologies Inc., 2005b). Reprinted from Inductively Coupled Plasma Mass Spectrometry – A Primer, p. 6, Copyright (2005), with permission from Agilent Technologies Inc.

The mass spectrum produced provides a simple and accurate qualitative representation of the sample. The magnitude of each peak is directly proportional to the concentration of an element in a sample (Agilent Technologies Inc., 2005b). Therefore, trace element quantitation for an unknown sample is conducted by comparing the ion signal with the signal intensities of known calibration or reference standards (Thomas, 2001-2002).

In addition to its many advantages, the detection capability of traditional quadrupole mass analysers for some critical elements is severely compromised by the formation of polyatomic spectral interferences generated either by argon, solvent, or sample-based

ionic species. Although tactics exist to minimise such interferences, including correction equations, as used in this research, or cool plasma technology and matrix separation, they cannot be completely eliminated. However, the relatively new collision/reaction cell technology has been developed to virtually stop the formation of many of these harmful species before they enter the mass analyser (Thomas, 2001-2002). These limitations and the desire to improve performance led to this development of collision/reaction cells in the late 1990s (Thomas, 2001-2002). The Agilent 7500ce ICP-MS instrumentation used herein is equipped with an Octopole Reaction System. The collision/reaction cell is positioned before the quadrupole mass analyser, where collision gas helium (He) or reaction gas hydrogen (H_2) can be introduced into the cell, as shown in Figure 1-7.

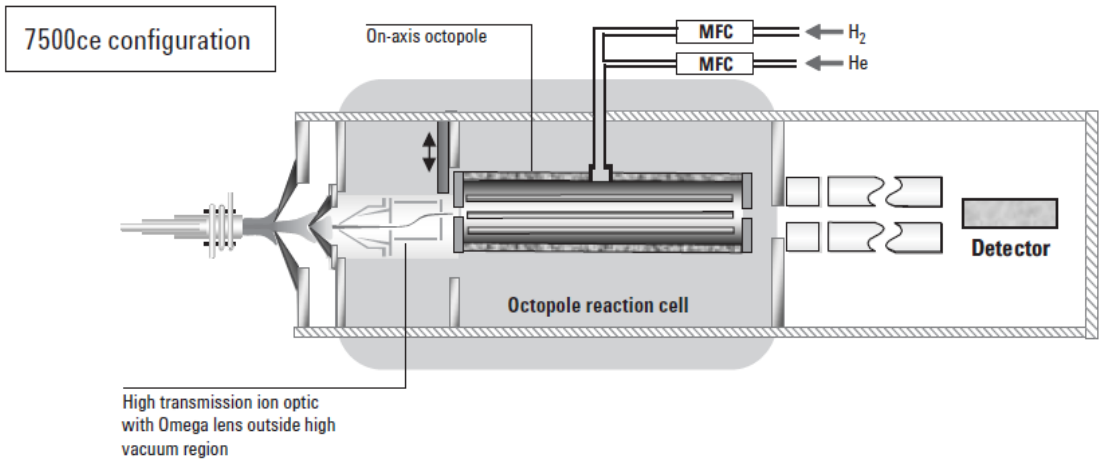


Figure 1-7. The ion optic and octopole configuration of the Agilent 7500ce ICP-MS instrument (Wilbur et al., 2004). Reprinted from Performance Characteristics of the Agilent 7500ce – The ORS Advantage for High Martrix Analysis, Part 1 or a 3 part series on Environmental Analysis, Wilbur et al., p. 2, Copyright (2004), with permission from Agilent Technologies Inc.

An example of the simple reactions that occur with the hydrogen gas to eliminate interferences on important elements like calcium, iron and selenium are as follows:

$$^{40}Ar^{+} + H_2 \rightarrow H_2^{+} + Ar \ (removes\ interference\ on\ ^{40}Ca^{+})$$

$$^{40}Ar_2^{+} + H_2 \rightarrow Ar_2H^{+} + H \ (removes\ interferences\ on\ ^{78}Se^{+}\ and\ ^{80}Se^{+})$$

$$^{40}Ar^{16}O^{+} + H_2 \rightarrow ArOH^{+} + H \ (removes\ interference\ on\ ^{56}Fe)$$

$$^{40}Ar^{16}O^{+} + H_2 \rightarrow H_2O^{+} + Ar \ (removes\ interference\ on\ ^{56}Fe)$$

In all reactions displayed here, the argon interference is removed from mass numbers 40, 56, 78 and 80 with no loss of analyte signal because calcium, iron and selenium do not react with hydrogen gas (H_2) (Wilbur et al., 2004). Similarly, the use of the helium collision

mode reduces or eliminates polyatomic interferences through nonreactive mechanisms (Wilbur et al., 2004). Some common polyatomic interferences are bound weakly enough for the collision energy between the polyatomic ion and the helium gas to break the polyatomic bond. Such polyatomic interferences include $NaAr^+$, which can interfere with the ^{63}Cu isotope in high sodium samples, and ArO^+, which interferes with iron (Wilbur et al., 2004). For these reasons, the use of an ICP-MS instrument with a collision/reaction cell is extremely valuable to a huge variety of analyses where the desire is to generate the most accurate and precise data.

The numerous advantages associated with Inductively Coupled Plasma-Mass Spectrometry make it an ideal technique to determine the concentrations of trace elements and heavy metals in water samples. The quantitative results produced from such analysis require the application of advanced statistical methods to manage the significant amount of data. As such, the application of chemometrics will provide a deeper understanding of the data that cannot be achieved with traditional univariate statistics.

1.1.4 Data Analysis – Chemometrics

Advances in instrumentation and chemical analyses have resulted in the continual increase in data production. More samples can be analysed in a smaller time frame, and more information can be collected from each sample. The quantitative data produced via ICP-MS are multivariate, defined as consisting of more than one variable. As in this research, information on 26 trace elements and heavy metals, or variables, was collected per sample analysed. Additional variables in the form of collision/reaction cell conditions: collision, reaction, or no gas data, were collected. Analysis of over 400 samples occurred from 2008 to 2013, and therefore, the data matrix generated for this research was substantial. Traditional statistics offers limited insights into such extensive data and as a result, chemometrics is employed in an attempt to reveal information otherwise overlooked.

Chemometrics is a term originally proposed in 1972 to describe the chemical field focussed on the application of mathematical, computational and logic methods to maximise the extraction of information from data and experimental measurements (Kokot & Ayoko, 2005; Kokot et al., 1998). Chemometrics has gained credibility over the decades, especially in the field of environmental analysis. As computational systems continue to become more

sophisticated, the depth of mathematics and statistics that can applied to any data matrix is greater than ever before. Chemometrics is now regarded as a separate experimental platform, in addition to the use of instrumentation for analysis. The interpretation of all types of chemical data can be furthered through the application of chemometrics. A few of the chemometric tools available now are pattern recognition, classification, discriminate analysis, calibration, prediction and multi-criteria decision making methods (MCDM).

Chemometrics goes beyond listing or tabulating different characteristics of the variables, using methods that can provide objective quantitative and/or qualitative investigations of the raw data. All chemometric analyses begin with a 2D data matrix consisting of objects and variables. Objects are usually displayed in rows, and variables in columns. Most data matrices undergo pre-treatment to remove weightings imposed on the variables by arbitrary units and to reduce random or irrelevant variations, known as noise. Data pre-treatment is an important issue because proper pre-processing of the data can be instrumental in developing better plots and models (Vandeginste, 1998).

The first step is to appraise the data with respect to completeness (Otto, 2007). Measurements that are below the detection limit were displayed as negative results in the output of the ICP-MS Agilent ChemStation software. Such measurements must be replaced by a positive value that is small relative to other values in the data set (Brereton, 2009). In this case, half of the Method Detection Limit (MDL) concentration was used to replace values that were below the MDL, where the MDL was determined to be one third of the lowest positive concentration returned for each variable. Brereton (2009) verifies that if there are few such values and no particular significance is placed on undetected variables, using half the minimum measurement is a good default choice.

Secondly, while it is known that missing data do not hinder mathematical analysis, missing data should never be replaced with zeros. If many measurements are missing altogether, it is necessary to consider whether samples or variables with missing values should be removed from the data matrix (Brereton, 2009). In order to retain all data, missing data can be replaced with the column/row mean, or in the worst case, a random number considered to be within the range of the column/row (Otto, 2007).

A basic form of pre-treatment is mean centering, which involves centering each variable by subtracting the column mean (Otto, 2007). Vandeginste (1998) explains that mean centring is so common that it is often not even considered as a form of data pre-treatment. Additionally, the different properties of a sample or an object are often represented in the

data, so the metric might differ from column to column to a great extent. These differences can be eliminated by scaling or standardising the data to similar ranges and variances (Otto, 2007). This is achieved by dividing each variable in the data set by the standard deviation of that variable. Auto-scaling is a combination of mean centering and standardisation, revealing data with zero mean and unit variance (Otto, 2007). This ensures that each variable has equal weight and is therefore a method of choice in many analyses. The effects of auto-scaling are demonstrated in Figure 1-8.

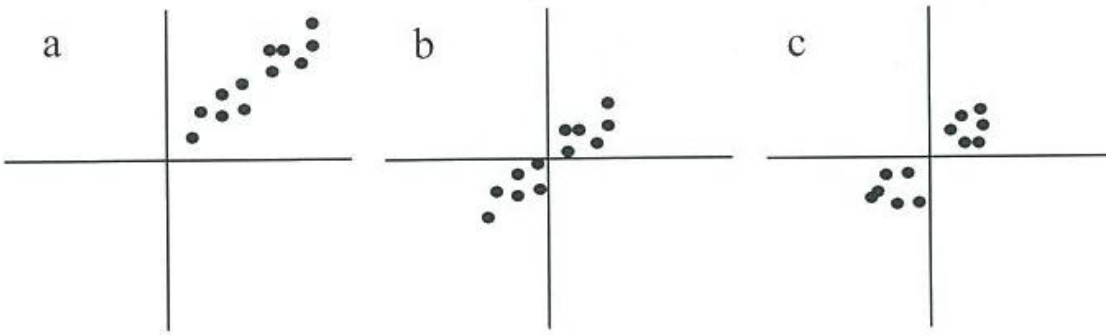


Figure 1-8. The original data is shown on plot A, plot B shows the data (mean) centred, and plot C shows the original data auto-scaled. Otto (2007) commented that autoscaling decreases within-group scatter and increases the perpendicular distance between groups, as seen here. Reprinted with permission from Matthias Otto: *Chemometrics - Statistics and Computer Application in Analytical Chemistry* (2nd ed.). p.124. 2007. Copyright Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.

Any pre-treatment of the data has to be applied in an identical manner to all current and future data (Vandeginste, 1998). Data pre-treatment options include but are not limited to mean centering, scaling (standardisation), normalisation, auto-scaling, and combinations of such techniques, to ensure the outcomes of chemometric analyses are objective comparisons and evaluations.

The exploratory nature of some chemometric techniques, particularly Principal Component Analysis (PCA), means that elucidation of patterns is often unsupervised. Therefore, method parameters are only loosely defined by the operator, and manipulating data to favour specific outcomes on the basis of previous research or background knowledge is avoided. A major advantage of chemometrics is that data processing has the ability to reveal features hidden in the structure of the raw data matrix; so in analytical chemistry, results are systematic, reproducible and amenable to visual display. However, Kokot et al. (1998) firmly state that chemometrics cannot fix poor sampling, calibration or validation, nor does it replace good analytical laboratory practice.

In addition to its frequent use in the field of environmental science, chemometrics is also prevalent in analytical chemistry, engineering, medical research and industry. Statistically significant parameters of factors tested can be successfully established by means of chemometrics, therefore minimising inclusion of insignificant data and producing objective, applicable results for all users. Overall, the outcomes of chemometrics are advantageous and generally include compression of large data sets through the elimination of redundancy and noise, the elucidation of patterns, ranking information, classification and prediction capabilities.

As previously mentioned in section 1.1.2, the role of trace elements and heavy metals in water is part of a complex interactive system that occurs throughout the water supply network. As a result, using chemometric technique Partial Least Squares (PLS) analysis to determine if metal ions can be predictors for water quality is an important aspect of this research because the cumulative nature of water quality means that any sudden changes in the concentrations of metal ions would be indicative of wider changes affecting the whole system.

The combination of the key concepts of water in South East Queensland, trace element and heavy metal toxicology, analytical techniques for environmental samples, and chemometrics evaluated in this section frames the background information required to understand the purpose and significance of this research.

1.2 Purpose

The purpose of this research is to investigate the concentration of trace elements and heavy metals in potable water of the greater Brisbane area. The combined use of Inductively Coupled Plasma – Mass Spectrometry and chemometrics will provide a deeper analysis and understanding of the variability in trace elements, all of which have been selected for their effect on human health, as well as their aesthetic nature in palatable potable water. The overall aim of this research is to identify different water sources, i.e. potable waters, raw water, treated water and mains water, and probable sources of trace element and heavy metal contamination in each of these sources, as well as to compare the data with the 2011 Australian Drinking Water Guidelines (ADWG).

The collection of historical data from 2008 to 2012 and data collected in 2013 specifically for this research will establish the effects, if any, that changing climatic conditions have on water quality. Finally, a model capable of predicting the trace element and heavy metal content of potable Brisbane water will be developed and based upon all trace element and heavy metal concentrations collected from various water sources, and across years that experienced extremes in climatic conditions. Therefore, this model will predict water quality for future years in terms of metal ion concentrations. Additionally, this method will reduce the number of variables required to determine water quality.

1.2.1 Research Questions

The questions that drive this research are as follows:

I. Can the heavy metal fingerprints of various water sources be distinguished?
    a. Is raw water easily distinguishable from treated water?
    b. Do the trace element and heavy metal concentrations in treated water change by the time it reaches our taps?
    c. Can different potable water sources (i.e. tap water, filtered water, bottled water, tank water) be distinguished by chemometric analysis of their trace element and heavy metal concentrations?
    d. Can the source of the water be determined from its trace metal profile?

II. Do changing climatic conditions affect potable water quality?

III. Which chemometric techniques can best maximise the elucidation of information collected from the data?

IV. Can metal ions be predictors for water quality?

1.2.2 Research Objectives

The following research objectives serve to answer the above research questions. The objectives are to:

- Compare and contrast the trace element and heavy metal fingerprints of the various sources and determine probable origins of contamination.

- Examine the effect (if any) of changes in climatic conditions through the analysis of historical and current data.
- Discriminate between the most relevant chemometric techniques used to analyse all data to determine usefulness.
- Establish if metal ions can be predictors for water quality through model development.

The purpose of these research questions and objectives is to demonstrate the significance of this research. The gap in the literature briefly described in the following section illustrates the area in which this research will make its original contribution to the field of water quality and environmental analysis.

1.3 Significance

There is comprehensive literature on the use of analytical techniques, particularly Inductively Coupled Plasma - Mass Spectrometry, coupled with a variety of chemometric techniques for the analysis of environmental samples including water, soil, foods and even wine. The successful combination of these techniques was a significant influence on the methodology used for this research.

Similarly, extensive research has been conducted for the determination of trace elements and heavy metals in waters, specifically for guidelines set by governing bodies like the World Health Organisation (WHO). The Australian Drinking Water Guidelines (ADWG) take the WHO Guidelines for Drinking Water Quality (2004) and subsequent addenda as their point of reference (National Health and Medical Research Council, 2011). Standard methods of analysis and additional information from the American Public Health Association (APHA) and the United States Environmental Protection Agency (US EPA), as well as independent research from reputable sources, are all considered by the National Health and Medical Research Council in the development of the 2011 ADWG.

Current literature demonstrates that monitoring the health of a city's waterways is seen as a priority worldwide. There are many studies that investigate anthropogenic influences and/or seasonal changes on naturally existing water bodies such as lakes, rivers and coastal bays, using fixed point sampling or even sediment analysis. In contrast, there is little, if any literature covering the collection and analysis of potable water from the consumers' tap.

Any investigations into water quality take place before water reaches the home, so there is no monitoring to indicate if tap water is safe after travelling from the treatment plant, through the distribution system and finally through a household plumbing system.

The 2011 ADWG suggest water quality sampling include the raw water source, in this case, the Brisbane River and dams that contribute to the water supply system; water entering the distribution system after disinfection or clarification, otherwise known as treated water; water at a variety of points throughout the distribution system and finally, at the consumers' tap. This suggestion was adopted for sample collection. As a result, raw water from the Brisbane River, its tributaries and several dams, treated water from Mt Crosby West Bank WTP, water from suburban mains water pipes and water from inside private residences were all collected.

This research is significant because the presence of trace elements and heavy metals is a vital aspect of water quality, and such an analysis has yet to be conducted on potable water sources from the home. The concentrations of trace elements and heavy metals in water can be accurately measured by ICP-MS. The use of chemometrics to further examine the data obtained will extract the maximum amount of information from the data to provide a better understanding of the quantitative results.

Additionally, as seen in the literature reviewed in Chapter Two, general factors influencing water quality such as lithogenic and anthropogenic contaminants, including agricultural and industrial contaminants, will be investigated for their contribution to the trace element and heavy metal content of potable Brisbane water. Therefore, source fingerprinting will be conducted for raw and potable water sources based on the characteristics of the collected samples. An analysis of the possible effect of climatic extremes on trace element and heavy metal content in water has not been undertaken and will also be investigated using the six year span of data now accumulated.

Therefore, the hypothesis for this research is that quantitative ICP-MS data modelled through the use of chemometrics will allow factors including water sources, sources of contaminants and effects of changing climatic conditions to be identified from trace element and heavy metal content of potable Brisbane water.

This hypothesis will be thoroughly investigated in the course of this research, the progression of which is outlined in the following section.

1.4 Thesis Outline

The remaining chapters will serve to comprehensively demonstrate the significance of this research. This will be achieved by the in-depth analysis and review of current literature in Chapter Two: Literature Review, followed by the explanation of the research design and methods, stemming from the literature review and methods previously applied at QUT, in Chapter Three: Research Design and Methodology. Next, Chapter Four: Results and Discussion will detail all results from this research and will relate the reasons such results were achieved to all previous chapters. Finally, the overall conclusions that can be drawn from this research will be summarised in Chapter Five: Summary and Conclusions, and future work or extensions of this research that may be undertaken will be outlined. All supplemental information will be located in Chapter Six: Appendices, followed by a complete list of references.

Chapter Two: Literature Review

This chapter analyses the literature according to four themes: Water, Toxicology, Inductively Coupled Plasma – Mass Spectrometry and chemometrics. There is extensive literature on each theme and in many cases, studies overlap. For example, as a highly regarded analytical technique, ICP-MS has previously been used to analyse water samples. Alternatively, chemometrics has been used in the analysis of environmental samples. In addition to analysing the literature in these areas, the implications previous work has on this research will be highlighted. The following review critically examines the literature to formulate arguments and identify gaps suitable for further research.

2.1 Water

Water is one of the most basic and essential constituents of the global environment (Komorowicz et al., 2010). The environment, as described by Voica et al. (2012), is an essential element of human existence. It is the result of natural elements – earth, air, water, climate, biosphere – with elements created by human activity. Humans rely heavily on water bodies for the variety of functions that they serve, inclusive of water supply, bathing, flood control, irrigation, transportation, power generation, fishery, recreation and tourism, as outlined by Xu et al. (2012) and Kumari et al. (2012). South East Queensland relies on the Brisbane River and its tributaries, which are utilised in each of these ways. With a note of warning, Damodhar and Reddy (2012) state that human interferences in the environment, through discharges from industrial or municipal sources, fertiliser applications, and liquid and solid waste disposal, can degrade water quality.

Water quality is a description of biological, chemical and physical characteristics of water in connection with intended use and a set of standards. Therefore, water quality assessment can be defined as the evaluation of biological, chemical and physical properties of water in reference to natural quality, human health effects and intended uses (Gazzaz et al., 2012). This research will focus solely on the chemical properties of water, specifically the presence of trace elements and heavy metals in drinking water. The set of standards used are the

2011 Australian Drinking Water Guidelines, developed by the National Health and Medical Research Council in collaboration with the Natural Resource Management Ministerial Council (National Health and Medical Research Council, 2011). Farooq et al. (2012) believe that the availability of good quality water is important for the prevention of disease and for improving quality of life.

But water fit for human consumption is not the only purpose for good quality water. The intended uses for treated water include other household applications, as well as industrial and agricultural operations. De Luca et al. (2008) state that water of adequate quantity and quality is required to meet the growing needs of domestic, agricultural and industrial uses. Berrittella et al. (2007) confirm the view of many others, that water is one of the basic and most precious resources, but observes that it is often in short supply, with estimates showing that the total amount of water available would be sufficient to provide the present world population with only the minimum amount of fresh water required. However, the uneven distribution of water (and population) among regions has made the adequate supply critical for a growing number of countries (Berrittella et al., 2007). Concern regarding adequate supply can only continue as water consumption for most uses is projected to increase by at least 50% by 2025, compared to levels in 1995 (Rosegrant et al., 2002 within Berrittella et al., 2007). Dawoud (2005) expands on this point, explaining that limited available surface water, high population growth and urbanisation development, deficient institutional arrangements, poor management practices, water depletion and deterioration of quality can all contribute to the gap between supply and demand for water.

Water as a global issue is emphasised in the literature and it is made clear that everyone must be mindful of the quantity of water consumed, especially in Australia, a country prone to the climatic extremes of drought and flood. The issue of water quantity is matched by that of quality of the available water. Johnson and Handmer (2002) define high quality drinking water as water that is odourless, clear and tastes good. These authors observe that consumers expect drinking water to be free of any health risks. Therefore, consumers expect the drinking water supplied to be both safe and appealing. Consequently, water supplied for domestic use must be analysed for quality and adherence to guidelines. Treated water supplied throughout South East Queensland undergoes the conventional treatment process of coagulation, flocculation, sedimentation and filtration, as previously described in section 1.1.1.1 of Chapter One. Chemicals added to the water at various stages enable each process to effectively remove potentially harmful contaminants in the

raw water entering the treatment plants (Seqwater, 2013h). Globally, treatment processes can vary, and Johnson and Handmer (2002) have explained that it is not in the interest of those in the water supply industry to exceed the minimum standard of quality imposed by the guidelines, because water is a non-substitutable resource and consumers cannot opt for a different commodity as they could, for example, for energy (Johnson & Handmer, 2002). Komorowicz et al. (2010) and De Luca et al. (2008) agree that the quality of water is predetermined by its intended uses, and that quality is largely influenced by natural processes and anthropogenic activities, as all water contains substances derived from the surrounding environment. The surrounding environment can therefore be separated into two contrasting sources of trace elements and heavy metals: natural (lithogenic) and anthropogenic. Anthropogenic influences are of greater interest in the literature as such effects are indicative of potentially deleterious long-term consequences.

Yang and Liu (2012) confirm that heavy metals are ubiquitous in the environment, naturally existing in small amounts in water, soil and food. The results of investigating river water quality allowed Vieira et al. (2012) to make the distinction between natural and anthropogenic sources of heavy metals. Natural contributions could be classified as climate variations, soil erosion, precipitation inputs and geomorphology of the area. Anthropogenic contributions include domestic, livestock and industrial effluent discharges from urban, agricultural and industrial activities respectively (Vieira et al., 2012). Anthropogenic activities such as rising urbanisation and industrialisation in the 21st century adversely affects water resources by the excessive use of toxic substances in industry or fertilisers in agriculture, as further exemplified by De Luca et al. (2008) and Haddad (2012). Rasheed et al. (2012) similarly attribute the occurrence of metal contaminants to rapid population growth, increased urbanisation and expansion of industrial activities, exploration and exploitation of natural resources, extension of irrigation among other modern agricultural practices, and a lack of environmental regulations.

Pinto et al. (2012) agree that anthropogenic contributions cause a strong impact on water quality, explaining that in recent years, the peri-urbanisation and the increased area of impervious surfaces in urban landscapes have led to the generation of large volumes of municipal runoff during rainy periods, which ends up in rivers. These authors also pointed out that treated and untreated sewage effluent, groundwater seepage carrying toxic leachates and nutrient-rich runoff originating from agricultural activities can profoundly alter water quality (Pinto et al., 2012). Mladenovic-Ranisavljevic et al. (2012) agree and also argue that harmful substances from farmland and heavy industries can severely undermine

the quality of the water. From the literature analysed here, it is clear that there are a multitude of sources from which trace elements and heavy metals may originate. Wang et al. (2012) concisely reiterate the views of the authors cited here, arguing that anthropogenic influences such as urbanisation, industrial and agricultural practices, chemical spills and accidents, dam construction, and natural processes like erosion and climatic conditions, could each affect water quality. However, the degree to which each factor contributes to water quality is unclear (Wang et al., 2012).

The focus of the literature detailed above has been on raw water sources, natural bodies of water such as lakes and rivers. The health of these water bodies is undeniably important as this water will be treated for human consumption. However, in addition to the health of waterways, the health of drinking water must also be scrutinised and thus far, the presence of trace elements and heavy metals in potable water has not received the attention it merits in the literature. Drinking water quality is a globally relevant issue that has not been widely researched at a local or national level.

The focus of this research is on trace element and heavy metal content of potable water. From this analysis of the literature, it is evident that some elements appear naturally in the environment and particular metals, such as calcium, sodium, potassium and magnesium are vital to human health. In natural aquatic ecosystems, metals occur at low concentrations, normally at the nanogram (*ng*) to microgram (µg) per litre level (Rasheed et al., 2012). In contrast, some metals are the result of urban run-off or atmospheric emission. These can be harmful in significant doses. In recent years, heavy metals found naturally in or entering the aquatic system have been widely studied for their persistence, toxicity and accumulation in the environment and their impact on human health. In the context of this work, trace metals are defined as inorganic compounds issued from natural and anthropogenic sources (Vystavna et al., 2012). Jiang et al. (2012) emphasise the danger trace elements and heavy metals may pose, because in contrast to organic contaminants, natural processes such as decomposition cannot remove heavy metals. In agreement with Jiang et al. (2012), Naseh et al. (2012) confirm that because of their toxicity, persistence and non-degradability, heavy metals are one of the largest threats to the environment, directly affecting flora, fauna and human health.

The preceding critical review of the literature on the theme of water has demonstrated that very few studies have addressed the issue of trace elements and heavy metals in drinking water. All of the authors illustrate the growing demand for water for various uses as a

global issue. For this reason, rapid and reliable methods for investigating water quality are essential to ensure the effectiveness of water treatment and management practices. The effects of the trace elements and heavy metals considered in this water quality investigation must first be explored.

2.2 Toxicology

The old adage, "everything in moderation", is applicable for the description of trace elements and heavy metals in potable water. With the exception of a few of the more toxic elements being studied, the literature analysed here demonstrates that many of the trace elements and heavy metals of interest are, in fact, essential to human health. However, Saleh et al. (2001) caution that all essential trace elements become toxic when their concentration levels become excessive (Yabanli, 2012). This is true for all water, from rivers and lakes to drinking water. Heavy metals present in nature are not usually dangerous for the environment because they are present in very small quantities. Heavy metals become pollutants in the environment only if they are present in large quantities (Voica et al., 2012). Elements arising primarily from natural contamination include arsenic, selenium, lead and uranium. Iron and manganese are also mentioned as frequent sources of aesthetic water quality problems, and these may lead consumers to use alternative water supplies that may not be safe with respect to microbial pathogens (WHO 2008 in National Health and Medical Research Council, 2011). Although this research is primarily concerned with human health effects resulting from excessive exposure to metals, it should be recognised that metals might also have deleterious effects on other animal species and plants (Nordberg et al., 2007).

There are numerous chemical forms, or species, of metals existing in waters. The toxicity and bioavailability of these different species of metals can vary significantly, as is exampled by the contrasting effects of chromium(III) and chromium(VI). Although the relationship between metal speciation, toxicity and bioavailability is complex, metals present as the free metal ion, or as weak complexes that can easily dissociate, are generally considered more bioavailable than metals in strong complexes or bound to particulate matter (Hamelink et al., 1994 within Markich et al., 2011). Metal bioavailability is primarily influenced by the pH and hardness (total Ca and Mg concentration) of water. The bioavailability of certain

metals can decrease with increasing hardness, as the calcium and magnesium ions compete for binding sites on cell membranes (Markich et al., 2001). Similarly, a decrease in pH may increase free metal ion concentrations, and encourage dissociation of metal complexes.

In this research, all concentrations of trace elements and heavy metals considered are total. Similarly, unless otherwise specified, the guideline values listed in the 2011 Australian Drinking Water Guidelines refer to the total concentration of the metallic element present, regardless of its form (National Health and Medical Research Council, 2011).

Pollution of the environment and human exposure to metallic elements may occur naturally, for example by erosion, or surface deposits of metal minerals, as well as from human activities such as mining, smelting, fossil fuel combustion, and industrial application of metals (Nordberg et al., 2007). The ways in which humans may be exposed to heavy metals includes inhalation, ingestion and skin contact. Yang and Liu (2012) believe that the ingestion of heavy metals from drinking water is an important route of exposure to consider. Many authors agree, with Nkono and Asubiojo (1997) and Turk and Alp (2010) confirming that drinking water plays a major role in the intake of some valuable and toxic trace elements in humans (Yabanli, 2012). Rahman et al. (2012) agree with exposure through consumption, and reiterate that the nature of activities in the vicinity of the reservoirs or rivers feeding water treatment plants have a profound effect on the trace element and heavy metal concentrations in that water. Metal trace elements, of which some can be essential for life, can also cause serious health problems because of their toxicity, persistence and accumulation in nature (Grellier et al., 2012 and references within). Health risks due to heavy metals at higher concentrations in water has been widely noticed by many researchers (Farooq et al., 2012) and as a result, the associated health risks of heavy metals has been thoroughly investigated by the numerous authors cited in this analysis of the literature.

Aluminium

Aluminium (Al) is a non-essential nutrient for humans (Toffaletti, 2005). It occurs naturally in the environment as silicates, oxides and hydroxides. Forms of aluminium that also occur in water include monomeric and polymeric hydroxyl species, various organic complexes and inorganic ligands, of which most but not all are soluble (WHO, 2013). Potable water supplies may contain greater concentrations of aluminium due to the use of aluminium salts in the water treatment process employed at Mt Crosby West Bank WTP. The guideline value in the 2011 ADWG is based on aesthetic problems caused by post-flocculation effects

(National Health and Medical Research Council, 2011). Although there is no health guideline for this element, Rasheed et al. (2012) noted that high aluminium concentrations have been implicated as a causative agent in various neurological disorders, including Alzheimer's disease. Lenntech B.V., a Dutch water treatment organisation, refers to aluminium as an innocent compound, but recognised that long lasting ingestion of significant concentrations of aluminium can lead to serious health effects, such as damage to the central nervous system, dementia, loss of memory and kidney problems (Lenntech BV, 2012). Aluminium is used in many industries to make a multitude of products. This metal easily forms alloys with copper, zinc, magnesium, manganese and silicon, and is important in transportation and building because of its light weight durability and strength (Lenntech BV, 2012).

Antimony

Antimony (Sb) is a common component of petroleum and coal, has numerous industrial applications, and is generally not used alone. It is found in lead storage batteries, solder, sheet and pipe metal and semiconductors; and antimony oxide compounds are found in textiles, rubber, adhesives, pigments and enamels (Australian Government Department of Sustainability, 2012). Especially relevant to this research is the fact that polyethelene terephthalate (PET), the plastic used for bottled waters and various storage containers, is produced by the polymerisation of the petroleum monomers terephthalic acid and ethylene glycol by antimony-based catalysts (Westerhoff et al., 2008). Antimony-based catalysts account for more than 90% of PET manufacture worldwide. Research conducted by Westerhoff et al., (2008) and Krachler and Shotyk (2008) found that antimony was leaching into water contained in PET bottles. All samples analysed were below the United States Environmental Protection Agency (US EPA) Maximum Contamination Level (MCL) of 6 µg/L, but Krachler and Shotyk (2008) pointed out that the reported levels of antimony in bottled water did not reflect the natural abundance of antimony in the source waters. Furthermore, it was noted that higher salt content in bottled water tended to result in higher antimony concentrations (Westerhoff et al., 2008).

Antimony is emitted to the environment through effluents from its aforementioned industrial applications, and also as a by-product of mining, metal smelting and the burning of coal. Humans are exposed to small background concentrations of antimony daily. Rahman et al. (2012) expand that airborne pollutants like antimony take some time to dissolve in water and then enter human beings through consumption. Soluble forms of

antimony tend to be quite mobile in water, whereas less soluble species are adsorbed onto particulate matter and sediments (WHO, 2013). The toxicity of antimony depends on its chemical form, where Sb(III) compounds have a greater toxicity than Sb(V) compounds. Ingesting large doses of antimony can cause nausea, vomiting and diarrhoea, and some compounds display similar toxic properties to those of arsenic (Australian Government Department of Sustainability, 2012). Antimony is a non-essential element for humans.

Arsenic

Arsenic (As) is an infamous heavy metal with severe effects on human health. It is known to be extremely poisonous to human beings and other animals (Reddy et al., 2012). Arsenic is widely distributed in the environment because of its natural and anthropogenic sources as well as its organic and inorganic forms (Voica et al., 2012). The Australian Government's National Pollutant Inventory (2012) confirms the use of arsenic in a variety of mining and manufacturing industries as well as its presence in the emissions of vehicles, aeroplanes, railway operations and boating or shipping. Rahman et al. (2012) confirm that as an airborne pollutant, arsenic takes time to dissociate in water, but is then consumed by humans. Arsenic exists in two oxidation states, As(V) and As(III). In well oxygenated surface waters, As(V) is generally the most common arsenic species; however, under reducing conditions, the most predominant form is As(III) (WHO, 2013). As(V) can also be reduced to As(III) in soils. In natural waters, these oxidation states occur in the triprotic arsenic acid and the monoprotic arsenious acid. For typical pH ranges in natural waters, arsenious acid, and therefore As(III), is the most important species (Ure & Davidson, 1995). Arsenic is described by Yang and Liu (2012) as an endocrine-disrupting chemical that affects the central nervous system. In addition, the NPI verified that this heavy metal decreases the production of red and white blood cells, can cause stomach, liver and kidney damage, is a recognised human carcinogen, and high concentrations result in death.

Barium

Barium (Ba) is the 14th most abundant element in the Earth's crust. It is used for barium-nickel alloys for items such as spark plug electrodes, vacuum tubes and fluorescent lamps, and other barium compounds are used for manufacturing paint, bricks, tiles, glass and rubber (Lenntech BV, 2012). The amounts of barium detected in water are usually not enough to raise health concerns, and consequently this metal is rarely discussed in literature. However, if very large amounts of barium are ingested, it may cause paralysis and in some cases death. Barium is not found free in nature, but exists in a number of

compounds. The most common forms, barium sulfate and barium carbonate, as well as chromate, fluoride, oxalate and phosphate compounds, are quite insoluble. In contrast, barium acetate, nitrate and halide compounds are soluble in water. The solubility of barium compounds increase as the pH level decreases (WHO, 2013). It is important to note that because of their water solubility, barium compounds can spread over great distances (Lenntech BV, 2012).

Beryllium

Elemental beryllium (Be) is not found in nature but as compounds in minerals rocks, soil, coal, oil and volcanic dust (Australian Government Department of Sustainability, 2012). Acidic groundwater encourages the dissolution of beryllium from minerals if they are present in the rock matrix (Rasheed et al., 2012). Of the simple beryllium compounds, only the chloride, fluoride, nitrate, phosphate and sulfate are soluble in natural waters. At neutral pH, most water soluble beryllium salts will be hydrolysed to insoluble beryllium hydroxide and beryllium oxide. As a result, only trace quantities of dissolved beryllium will remain. Therefore, beryllium is rarely, if ever, found in drinking water at concentrations of concern (WHO, 2013). If ingested or inhaled, beryllium can be irritating to the respiratory tract, eyes and skin. Irritation of the respiratory tract by any toxic chemical is often referred to as chemical pneumonia. The NPI infers that exposure to beryllium mostly occurs in specialised workplaces and is not a major cause for concern in drinking water.

Cadmium

Cadmium (Cd) is a metal that is chemically similar to zinc, and occurs naturally with zinc and lead in sulfide ores. The solubility of cadmium is largely influenced by the acidity of water; therefore, at neutral pH levels, cadmium is mainly found in suspended particulate matter and sediments (WHO, 2013). Cadmium is considered an anthropogenic indicator of the industrial impact of an area. Pathways to the environment include industrial processes like coal combustion, smelters, iron and steel mills, electroplating and production of chemicals (Vystavna et al., 2012). The National Pollutant Inventory (Australian Government Department of Sustainability, 2012) adds that cadmium is also found in phosphate fertilisers, batteries, PVC products and tobacco. Watanabe et al. (2012) emphasise cadmium as a wide-spread environmental pollutant with insidious toxicity on kidney and bone, typically after long-term exposures even at low levels. Damodhar and Reddy (2012) similarly argue that cadmium is one of the most dangerous pollutants due to its potential toxic effects and could cause renal disease and cancer.

Calcium

Calcium (Ca) is an essential trace element for human health found naturally in water. It is the most abundant element in the human body. Calcium is the main constituent of bones and teeth, and it has key metabolic functions (Lenntech BV, 2012). Li and Zhang (2012) highlight calcium as an essential nutrient for brain development and function. A lack of calcium is one of the main causes of osteoporosis and a daily intake of 1000 mg of calcium is needed to preserve bone mass in normal conditions (Lenntech BV, 2012). Calcium is also used in industrial and agricultural applications as an alloy and a deoxidiser, and is present in various construction materials such as bricks, cement and concrete.

Chromium

Chromium (Cr) is a naturally occurring element and is analysed in two forms in the literature: chromium(III) and chromium(VI). Speciation of Cr(III) and Cr(VI) is an existing challenge within analytical chemistry. As a result, the WHO, US EPA and ADWG all have guidelines for 'total chromium' in various waters. Speciation of an element in a water sample may be defined as the determination of the concentration of different physicochemical forms of the element that together make up its total concentration in the sample (Kumaresan and Riyazuddin, 2001 in Rakhunde et al., 2011).

Chromium can exist in all oxidation states from 0 to VI, where Cr(III) is the most stable state. In general, Cr(VI) predominates under oxidising conditions, and Cr(III) predominates under reducing conditions (Rakhunde et al., 2011). The distribution of compounds containing Cr(III) and Cr(VI) depends on the redox potential, pH, presence of oxidising or reducing compounds, kinetics of the redox reactions, formation of Cr(III) complexes or insoluble Cr(III) salts, and total chromium concentration. Cr(VI) is thermodynamically stable in pure water for natural pH and redox conditions, whereas in more acidic waters and in the presence of readily reducible organic substances, Cr(III) species are predominant (Rakhunde et al., 2011). In general, Cr(VI) salts are more soluble than Cr(III) salts, therefore Cr(VI) is relatively mobile (WHO, 2003 in Rakhunde et al., 2011). Rakhunde et al. (2001) also recognise that the presence and concentration of chromium forms in discharged eluents depend mainly on the chromium compounds applied in the industrial process, on pH and other organic or inorganic wastes coming from the material processing.

Voica et al. (2012) infers that chromium exposure for humans is due to anthropogenic sources, largely coming from its wide application in industrial fields, and Vystavna et al.

(2012) agree, naming chromium as an anthropogenic indicator of the industrial impact on a water system. Rahman et al. (2012) are also of the belief that chromium is discharged from industrial areas. Chromium and its salts are used in the leather tanning industry, the manufacture of catalysts, pigments and paints, fungicides, the ceramic and glass industry, photography, chrome alloy and chromium metal production, chrome plating and corrosion control (Rakhunde et al., 2011). Rasheed et al. (2012) report that this heavy metal is not acutely toxic to humans, and state that Cr(VI) is more toxic than Cr(III) because of its high absorption rate through the intestinal tract. Chromium(VI) may be reduced to chromium(III) in the natural environment, thereby reducing the toxic impact of chromium discharges.

Chromium(VI) is very toxic to humans and is a known carcinogen, but in contrast, chromium(III) is a nutrient essential to the proper function of living organisms. Cr(III) combines with various enzymes in transforming sugar, protein and fat. In contrast, Cr(VI) is a human carcinogen and may cause various other health problems such as skin rashes, upset stomachs and ulcers, weakened immune systems, kidney and liver damage, alteration of genetic material, and death (Rakhunde et al., 2011). An incident of contamination of drinking water by hexavalent chromium (Cr(VI)) in Hinkley, Southern California was bought to the world's attention through the involvement of lawyer Erin Brockovich (Brockovich, 2014). This story and the carcinogenic effects of Cr(VI) received considerable attention thanks to the movie "Erin Brockovich" starring Julia Roberts (Soderbergh, 2000). Hexavalent chromium leeched into the groundwater from the evaporating ponds of a Pacific Gas and Electric power plant. The levels of Cr(VI) alone significantly exceeded the Maximum Contaminant Level (MCL) for total chromium (i.e. Cr(III) and Cr(VI)) set by the US EPA. Despite the risks associated with Cr(VI), Haddad (2012) has commented that chromium from food and beverages is poorly absorbed and the toxicity of chromium is mainly due to this heavy metal being absorbed by the respiratory tract, and also to a certain extent through the skin.

Cobalt

There is very little consideration of cobalt (Co) in the literature. It is a metal that occurs naturally in a variety of forms and is found in soil, seawater, smoke from bush or forest fires, as well as anthropogenic sources like the production of alloys and the mining or refining of other metals (Australian Government Department of Sustainability, 2012). It is a component in the vitamin B-12 and as such is both beneficial and harmful to humans.

Cobalt may be used in the treatment of anaemia but can also have adverse effects on the respiratory system, the skin, kidneys and heart (Australian Government Department of Sustainability, 2012).

Copper

Copper (Cu) is both a micronutrient and toxicant depending on the dose (Voica et al., 2012). Copper is abundant in nature and has various natural pathways, including rock weathering, soil erosion and animal waste (Vystavna et al., 2012). The fate of elemental copper in water is complex, and depends on pH, dissolved oxygen levels and the presence of oxidising agents. In most instances, the copper(I) ion will be oxidised to the copper(II) ion. The copper(II) ion is the more common oxidation state in natural waters and will form insoluble copper(II) hydroxide and copper(II) carbonate compounds. Other common copper(II) compounds, including acetate, chloride, nitrate and sulfate, are water soluble (WHO, 2013).

Copper also has a plethora of anthropogenic sources, such as copper pipes and roofing, sewage, petroleum refining, chemical manufacture, electricity supply, cement, plaster and concrete products, even glass and paper products to name just a few (Australian Government Department of Sustainability, 2012). The National Pollutant Inventory recognises mining and metal manufacturing as the largest sources of copper in Australia. It is also important to note that copper pipes are still in widespread use in household water systems throughout Brisbane. The extensive range of copper sources allows its use as an anthropogenic indicator of the industrial impact of an area (Vystavna et al., 2012). One to two milligrams is the recommended daily intake of copper to maintain good health. In contrast, high levels of copper can be harmful to health. Ingesting significantly high levels can cause nausea, vomiting and diarrhoea and may lead to kidney and liver damage (Australian Government Department of Sustainability, 2012).

Iron

By mass, iron (Fe) is the most abundant element on Earth. Iron exists in oxic environments as Fe(III), and in anoxic environments as Fe(II) (Nordberg et al., 2007). It is an essential metal for almost all living things (Lenntech BV, 2012). Iron is an essential nutrient for brain development and function (Li & Zhang, 2012). It is also an essential part of haemoglobin, the red colouring agent of the blood that transports oxygen throughout the body (Lenntech BV, 2012; Nordberg et al., 2007). In contrast to the majority of other heavy metals, the most common problem is not ingesting dangerously high amounts of iron, but rather, iron

deficiency. Iron deficiency leads to anaemia, resulting in tiredness, headaches and loss of concentration, and also affects the immune system (Lenntech BV, 2012). However Voica et al. (2012) warn that iron poisoning can affect the central nervous system.

Many iron compounds are soluble in water and are therefore easily consumed. Natural processes include the weathering of iron minerals or ores that release iron into the water. Elemental iron is rarely found in nature, as the iron ions Fe(II) and Fe(III) readily combine with compounds containing oxygen and sulfur to form oxides, hydroxides, carbonates and sulfides. In drinking water supplies, Fe(II) salts are unstable and are precipitated as insoluble iron(III) hydroxide (WHO, 2013). Iron is the most used of all metals, with its applications ranging from food containers to cars, screwdrivers to washing machines, metal alloys and cargo ships to paper staples (Lenntech BV, 2012).

Lead

Lead (Pb) is one of the most abundant heavy metals in nature (Voica et al., 2012). It is an essential nutrient, but can also be toxic for humans. Voica et al. (2012) pointed out that lead residence time in blood and soft tissue is a month, but is fifty years in the liver. Lead poisoning affects the central nervous system, can cause miscarriage and infertility (Al-Sabbak et al., 2012; Kahraman et al., 2012), and can affect almost every organ and system in the body (Australian Government Department of Sustainability, 2012). Numerous studies in children have confirmed the adverse effects of lead exposure on cognition and other neurological functions, thereby constituting a serious public health problem in a global perspective (Nordberg et al., 2007). Nordberg et al. (2007) report the prevalent opinion that there is an inverse relationship between IQ and blood lead levels, although the magnitude of this effect is often debated.

Voica et al. (2012) believe that the most important anthropogenic source of lead in the environment is the combustion of gasoline containing lead. However, leaded petrol was phased out of use by the early 2000s in Australia. Lead has absolutely no beneficial effects on human health, and lead emissions from motor vehicles contributed about 90% of airborne lead in Australia's urban areas (Department of the Environment & Heritage, 2001). Reducing the use of lead in petrol therefore reduces airborne lead, and lead in street and household dust. When the use of leaded petrol was prominent in the 1970s, the anthropogenic emissions of lead to the atmosphere were estimated to be between 400 000 and 500 000 tonnes, a value exceeding the natural cycling of lead by approximately

100 times (Lantzy & Mackenzie, 1979; Nriagu, 1989 within Nordberg et al., 2007). Consequently, the anthropogenic contamination of the environment with lead has exceeded that of any other metal.

Airborne pollutants like lead can behave in multiple ways once they are deposited in water. Lead is effectively removed from the water column by adsorption to organic matter, precipitation and reactions with hydrous iron and manganese oxide. Acidic conditions can result in the dissolution of lead already bound to sediment or particulate matter (US EPA, 2013b). Water soluble lead compounds, such as lead carbonate, nitrate and acetate, can then be consumed by humans (Rahman et al., 2012). Rocks and soil are natural sources of lead, while other anthropogenic sources include industrial effluent, with the National Pollutant Inventory highlighting mining and manufacturing as the largest source of lead emissions in Australia (Australian Government Department of Sustainability, 2012).

Magnesium

Magnesium (Mg) is an essential nutrient in brain development and function (Li & Zhang, 2012), muscle contraction and DNA replication, and is an ingredient of many enzymes (Lenntech BV, 2012). It is unusual to introduce legal limits for magnesium in drinking water as there is no scientific evidence of magnesium toxicity (Lenntech BV, 2012). These same authors state that there are no known cases of magnesium poisoning, but large oral doses may cause vomiting and diarrhoea. Rasheed et al. (2012) further explain that excess magnesium concentration can lead to changes in mental status, loss of appetite, extremely low blood pressure and irregular heart beat. Magnesium is abundant in the Earth's crust, and its components are widely used in industry and agriculture. Due to magnesium's low density, it is used in countless engineering applications where the weight of the product is an important consideration (Lenntech BV, 2012).

Manganese

The National Pollutant Inventory (2012), Rasheed et al. (2012) and Li and Zhang (2012) all agree that manganese (Mn) is an essential trace element. Rasheed et al. (2012) describe manganese as a vital micronutrient that contributes to the normal development of connective tissues and is necessary for respiratory enzymes. Manganese is present in high concentrations in the kidney, liver and pancreas, and in very large doses may cause some diseases and liver damage (Rasheed et al., 2012). The National Pollutant Inventory defends the view of Rasheed et al. (2012), stating that naturally occurring concentrations are hardly

toxic, and relatively large doses can be tolerated without adverse effects. Although a naturally occurring element, manganese is not naturally found in its metallic form (Australian Government Department of Sustainability, 2012). Manganese ores very often occur together with iron ores, and Reddy et al. (2012) add that manganese is present most frequently as a manganous ion and in iron-bearing waters. Manganese can be released during the mining, crushing and smelting of ores and can be found in batteries, some mineral supplements, fertilisers and disinfectants (Australian Government Department of Sustainability, 2012).

In aquatic environments, manganese occurs in both soluble (Mn^{2+}) and suspended (MnO_2) forms, depending on pH, anions present and oxidation-reduction potential (WHO, 2013). The manganese(II) ion predominates in most water at pH 4-7, but more highly oxidised forms may occur at higher pH values or result from microbial oxidation (ATSDR, 2000 within WHO, 2013). The soluble Mn(II) ion can be oxidised to insoluble manganese dioxide (MnO_2) and then removed by coagulation, flocculation, sedimentation and filtration (Raveendran et al., 2001). Oxidation in dams and water treatment facilities can be achieved by aeration or the addition of oxidising agents such as chlorine, sodium hypochlorite or potassium permanganate (Raveendran et al., 2001). However, MnO_2 deposits that have settled in the catchment area cannot be readily removed by these treatment processes. This is a particular problem when the water takeoff point is at the bottom of the dam. If not oxidised, Mn(II) ions will escape into the water supply system. Once in the system, the Mn(II) ion is gradually oxidised to insoluble MnO_2 (Raveendran et al., 2001).

In addition to aeration or oxidising agents, the aforementioned microbial oxidation of manganese refers to a phylogenetically diverse group of bacteria that are ubiquitous in the environment, and are characterised by the ability to oxidise soluble Mn(II) to insoluble manganese oxides (Nealson, 2006). The result is an accumulation of extracellular deposits of insoluble brown or black manganese oxides. A by-product of the redox processes of manganese-oxidising bacteria is hydrogen sulfide (H_2S) gas, which has the characteristic odour of rotten eggs. Toxic levels of manganese and manganese oxide deposits can therefore be a problem in municipal water supplies.

Manganese deposits may occur in water pipes (Nealson, 2006), and these brown/black deposits and the foul odour associated with this process are problematic for residents and, consequently, water suppliers. In particular, high water use in the warm summer months (December to March) can slough off MnO_2 deposits from piping. Locally, consumers

supplied by the Hinze Dam on the Gold Coast have, on past occasions, reported high levels of manganese in their water supply. In addition to poor aesthetic quality of drinking water supplied to residents, the brown/black discolouration of the water causes staining of fixtures, equipment, laundry, and even swimming pools (Sly et al., 1990). The ADWG therefore enforce both aesthetic and health related guidelines in order to monitor the levels of manganese present in drinking water.

Mercury

Mercury (Hg) is probably the most notorious heavy metal. It is a naturally occurring element that is released into the atmosphere by evaporation from soils, from volcanic activity and from the burning of fossil fuels (Australian Government Department of Sustainability, 2012). Precious metal mining operations, photographic processing facilities, municipal landfill, sewage and chemical manufacturing may also emit mercury to land and water (Australian Government Department of Sustainability, 2012). On a worldwide scale, the artisanal and small-scale gold mining sector is responsible for the largest releases of mercury into the environment, releasing approximately 400 tonnes of airborne elemental mercury each year (US EPA, 2013a). The solubility of mercury compounds in water varies. Elemental mercury is insoluble, and mercury(I) chloride and sulfide have very low solubility while mercury(II) chloride is readily soluble in water (WHO, 2013). Additionally, methylation of inorganic mercury is an important process in water and occurs in both fresh and sea waters; however, the World Health Organisation (2013) state that there have been no reports of methylmercury found in drinking water.

The central nervous system is sensitive to all forms of mercury, a fact confirmed by Yang and Liu (2012), who label it an endocrine-disrupting chemical, while Li and Zhang (2012) similarly believe that exposure to mercury is associated with a significantly increased risk of stroke. Mercury also accumulates in the body and exposure to high levels of any type of mercury can permanently damage the brain, kidneys and developing foetus (Australian Government Department of Sustainability, 2012).

Molybdenum

Molybdenum (Mo) is described as moderately poisonous to humans and other animals by Reddy et al. (2012). The main features of molybdenum exposure include joint pain in the knees, hands and feet, articular deformities, erythema and oedema of the joint areas (Lenntech BV, 2012). It is known to be more soluble in alkaline soils and is an essential

trace element in plant nutrition. Molybdenum does not occur naturally as a free metal, but exists in ores. Molybdenum is mined principally from molybdenite, MoS_2, and is also a byproduct of copper and tungsten mining. MoS_2 is sparingly soluble and is readily oxidised to more soluble molybdates, MoO_4^{2-}, which are stable in water in the absence of a reducing agent (Asmanguljan, 1965 within WHO, 2013). Molybdenum is also used in alloys, electrodes and catalysts and is most notably a valuable catalyst for the refining of petroleum (Lenntech BV, 2012).

Nickel

According to the National Pollutant Inventory (2012), the major sources of nickel (Ni) exposure for most people are consuming food and drinking water which contain natural amounts of nickel. Nickel predominantly occurs as the nickel hexahydrate ion ($Ni(H_2O)_6^{2+}$) in natural waters at pH 5-9 (IPCS, 1991 within WHO 2013). The WHO (2013) characterise several nickel compounds, such as the acetate, chloride, nitrate and sulfate salts, as water soluble; while carbonates and hydroxides are far less soluble, and sulfides, disulfides and oxides are practically insoluble. A small amount of nickel is essential for humans, however, a lack of nickel has not been found to effect the health of humans, and very large amounts must be ingested to show adverse health effects (Australian Government Department of Sustainability, 2012). Voica et al. (2012) believes that nickel poisoning affects the central nervous system, while Li and Zhang (2012) similarly argue that exposure to nickel is associated with a significant increase in the risk of a stroke. Nickel can indicate heavy fuel oil combustion (Cizdziel, 2010) and can be found in the effluents of various industrial processes: smelting, refining, alloy production and plating, and in municipal sewage (Reddy et al., 2012).

Potassium

Potassium (K) occurs in the Earth's crust as minerals and it is released into the environment through the weathering process (Lenntech BV, 2012). Potassium is found in fertilisers, potassium carbonate is used in glass manufacture and potassium hydroxide is used in liquid soaps and detergents. Potassium is a dietary requirement for humans and plays vital roles in nerve stimulus, muscle contractions, blood pressure regulation and cellular function, protecting the heart and arteries, perhaps even preventing cardiovascular disease (Lenntech BV, 2012). Li and Zhang (2012) add that it is an essential nutrient for brain development and function, particularly for the generation of electrical potentials. However, Rasheed et al. (2012) warn that increased exposure to potassium could result in

significant health effects in people with conditions such as kidney disease, heart and coronary artery disease, hypertension and diabetes. Potassium balance is regulated by the kidneys, and while potassium shortages are rare, it is believed to lead to depression, confusion, muscle weakness and heart rhythm disorder (Lenntech BV, 2012).

Selenium

Selenium (Se) has the dual role of an essential element at low concentrations and a toxicant at high concentrations (Voica et al., 2012). Li and Zhang (2012) describe selenium as an essential nutrient in brain development and function. The National Pollutant Inventory (2012) agrees and infer that the daily requirement of selenium is met by the selenium found naturally in food and drinking water. Diets lacking selenium have resulted in heart problems and muscle pain, whereas too much selenium can result in excessive tooth decay, discolouration of the skin and teeth, brittle hair, deformed nails, fatigue, irritability, depression and pallor (Australian Government Department of Sustainability, 2012). Selenium occurs naturally in water from the weathering of soils and rocks, and is also enriched in coal. Elemental selenium and selenides are insoluble in water, however, salts of acids formed on contact with water, known as selenites and selenates, are usually soluble in water (Nordberg et al., 2007). Concentrations of selenium increase at high and low pH as a result of conversion into compounds of greater water solubility (WHO, 2013). Airborne pollutants like selenium take some time to dissociate in water, but are then consumed by humans (Rahman et al., 2012). Anthropogenic sources of selenium include coal combustion (Cizdziel, 2010) and effluent from industrial process such as metal refining and glass and ceramics manufacturing (Australian Government Department of Sustainability, 2012; Reddy et al., 2012).

Silver

Silver (Ag) has various urban and industrial anthropogenic sources: the photographic industry, coins and jewellery production, batteries, brazing alloys, electroplating, electrical controls and conductors, medical service, nanotechnology and paints (Vystavna et al., 2012). Also found naturally as crystals, a compact mass or in ores, the principal use of silver is as a precious metal (Lenntech BV, 2012). Because of the wide range of anthropogenic uses for silver, Vystavna, Le Coustumer and Huneau (2012) propose silver as an anthropogenic indicator of industrial activity. Silver is not a dietary requirement for humans and Lenntech BV (2012) reports that of the 20-80 µg daily intake of silver, only 10% is absorbed. The most important silver compounds from the point of view of drinking

water are silver nitrate and silver chloride (WHO, 2013). Silver compounds can be slowly absorbed in body tissues and are labelled as moderately toxic, causing stomach discomfort, nausea, vomiting, diarrhoea and narcosis if large amounts are ingested (Lenntech BV, 2012).

Sodium

Sodium (Na) is the sixth most abundant element in the Earth's crust and is therefore naturally present in ground and surface waters from the weathering of soils and rocks (Lenntech BV, 2012). Sodium salts, such as sodium chloride, carbonate, hypochlorite and metasilicate, are generally highly soluble in water (WHO, 2013). Anthropogenic sources of sodium include its use in metallurgy and its many industrial purposes, resulting in sodium in industrial and urban effluent. Sodium is a vital dietary mineral involved in the transmission of nerve impulses and maintenance of water acid-base balance within the body.

Controversy surrounds the amount of sodium required in a healthy diet. The Heart Foundation (2014) recommends that the average adult should aim to consume less than 2300 mg of sodium (equivalent to 6 grams of salt) per day. High intakes of sodium can increase blood pressure and therefore the risk of cardiovascular disease including heart, stroke and blood vessel disease (National Heart Foundation of Australia, 2014). Excessive intake may also cause acute effects like nausea, vomiting, inflammatory reaction in the GI tract, thirst, muscular twitching, convulsions and possibly death (Rasheed et al., 2012). These authors also highlight hypertension as an effect of long term low level exposure, as well as possible disturbances to the central nervous system such as convulsions, confusion and pulmonary oedema (US EPA, 2003 within Rasheed et al., 2012). In contrast, a shortage of sodium in the diet can result in dehydration, convulsion, muscle paralysis, decreased growth and general numbness (Lenntech BV, 2012).

Thallium

Thallium (Tl) and its compounds are highly toxic and as such, are not required in the human diet. The most recognisable form of thallium is thallium sulfate, a compound found in rat poison prior to the early 1970s. Effects of thallium poisoning include hair loss, stomach aches, damage to the central nervous system such as trembling, paralysis and behavioural changes, and cancer. Consequences of thallium uptake through food and water are nerve and joint pains, while the accumulation of thallium in the body can result in many chronic

symptoms like tiredness, headaches, depression, lack of appetite, leg pains and disturbances of sight (Lenntech BV, 2012).

Interestingly, these authors point out that thallium is not a rare element, and is 10 times more abundant than silver. It occurs widely in the environment and is partially soluble in water, allowing movement throughout soils and water ways (Lenntech BV, 2012). Thallium is applied in electro-technical and chemical industries (Lenntech BV, 2012) and is obtained through the smelting of iron and zinc ores and as a by-product of sulfuric acid production (Chemicool, 2013). Besides its use in these specific industries, there are very few anthropogenic sources of thallium.

Thorium

A heavy metal rarely discussed in relation to water quality is thorium (Th). Naturally occurring thorium is generally insoluble, and is not circulated throughout the environment (Lenntech BV, 2012). It is radioactive and, like uranium, could be a source of nuclear fuel. It is also used in the manufacture of refractory materials for metallurgy and as an alloying element in the electrical industry (Lenntech BV, 2012). Thorium is surprisingly abundant, found nearly everywhere on Earth and as a result, everyone will absorb thorium through food and drinking water. There is no biological role for thorium and it is radioactive in all its forms. Because thorium compounds are very insoluble, 99.98% of ingested thorium will pass through the body unabsorbed (Krachler & Shotyk, 2009). If, however unlikely, large amounts of thorium are ingested, three quarters of the 0.02% which is absorbed will be stored in bone, and these authors warn that due to its radioactivity, it can become cancerous many years later (Emsley, 2001 within Krachler & Shotyk, 2009; Lenntech BV, 2012).

Vanadium

Vanadium (V) is a naturally occurring element that is never found unbound in nature. Vanadium occurs in about 65 different minerals and is obtained as a by-product of other ores (Lenntech BV, 2012). It also occurs in carbon containing deposits such as crude oil and coal, and the presence of vanadium can indicate heavy oil fuel combustion (Cizdziel, 2010). Vanadium is abundant in most soils, thus water mediated transport is an important way in which this element is redistributed throughout the environment because its compounds are generally water soluble. Vanadium is used in industry as a steel additive, as alloys in nuclear reactors, and vanadium oxide is used as a catalyst in sulfuric acid and ceramic

production (Lenntech BV, 2012). As such, vanadium can be found in industrial waste water discharge (Reddy et al., 2012). The health implications of high intake of vanadium illustrated by these authors includes irritation of throat, eyes and nasal cavity, headaches, damage to the central nervous system and bleeding of the liver and kidneys. However, they continue that vanadium compounds are not usually regarded as a serious hazard.

Uranium

Uranium (U) is radioactive and is present in background levels throughout the environment. Humans are exposed to uranium through food, water, soil and air, yet there are no harmful radiation effects detected at natural levels (Lenntech BV, 2012). Uranium in water is leached from soil, granites, and various other mineral deposits, with only a very small amount of uranium from the air settling in water. In nature, hexavalent uranium is commonly associated with oxygen as the uranly ion, UO_2^{2+}, which is insoluble in water (WHO, 2013). Phosphate fertilisers, made from material typically high in uranium, and industrial activities like mining and nuclear energy production, add uranium to soil (Lenntech BV, 2012). It is interesting to note that in 2003, the US Food and Drug Administration (FDA) amended previous guidelines to allow concentrations of up to 30 µg/L (or parts per billion) in bottled water (Hasslberger). In contrast, the maximum concentration of uranium acceptable in any potable water in Australia is 17 µg/L. Additionally, Australia has the potential to be a major exporter of uranium. There are multiple mines that have been depleted and/or closed and many more sites throughout the country that could be uranium mines in the future.

Currently, active mines include the Olympic Dam mine and Beverly Uranium mine in South Australia, and the Ranger Uranium mine in the Northern Territory. There is some concern from residents in the areas surrounding the active mine sites regarding contamination of surface and ground waters. Dispersion or migration of radionuclides through groundwater systems, primarily radionuclides with relatively long half-lives like uranium isotopes 238 and 234 (U-238 and U-234), is considered one of the most important pathways for potential environmental impact from uranium mining activities (Australian Government Department of the Environment, 2014a). Furthermore, surface water can transport these radioactive species from either a controlled release from a working mine site, or an uncontrolled release, which may be due to erosion of material from a site or surface expression of groundwater containing radionuclides (Australian Government Department of the Environment, 2014b). Radionuclides can then incorporate into traditional foodstuffs and

the water column. If exposed to high levels of uranium, chemical effects may cause kidney disease, whilst long term exposure to the radioactive decay of enriched uranium may cause cancer to develop.

Zinc

Reddy et al. (2012) describe zinc (Zn) as an essential metal. Human cells employ metals such as zinc to control significant metabolism and signalling functions, making them essential for life (Haddad, 2012). Li and Zhang (2012) also emphasise its role in brain development and function, particularly in regulating brain excitability and neurotransmission, while Yang and Liu (2012) indicate its importance as a structural and catalytic component of enzymes in the human body. Zinc is present in natural waters and Voica et al. (2012) recommend that zinc concentrations in drinking water remain below 5 mg/L, as at greater concentrations water can become cloudy and take on an astringent taste due to the water soluble zinc sulfate salt (WHO, 2013). The aesthetic guideline for zinc within the 2011 Australian Drinking Water Guidelines is in agreement with these authors at 3 mg/L (National Health and Medical Research Council, 2011). The National Pollutant Inventory (2012) states that either too little or too much zinc can be harmful, causing health problems. Too little zinc can result in a loss of appetite, a decreased sense of taste and smell, and damage to the immune system. A diet consisting of too much zinc can cause stomach cramps, vomiting or even anaemia and pancreas damage. Too much zinc may also interfere with the body's ability to absorb and use other essential elements like copper and iron (Australian Government Department of Sustainability, 2012). Naturally found in the environment, zinc also has a variety of anthropogenic uses and sources. Zinc is heavily used in galvanising, where corrosion of galvanised structures can release zinc into water. The most widely used zinc compound, zinc oxide, is insoluble in water (WHO, 2013). Zinc can also enter the aquatic environment through urban waste and industrial effluent (Reddy et al., 2012).

From the toxicological information gleaned from the literature, the suggestion by Voica et al. (2012) that traces of metal ions have important roles in a wide spectrum of functions of life is easily understood. Metal ions have been shown to occur naturally, as well as from a variety of anthropogenic sources summarised by Said et al. (2012): discharge of industrial or sewage effluents, domestic waste water, periodic precipitation contaminated with airborne pollutants, transport, mining, burning of fossil fuels, and fertilisers and pesticides in agriculture. Among the kinds of contaminants, heavy metals have great potential

biological risks (Jiang et al., 2012). Casarett and Doull (2007) acknowledge that toxic effects in a biological system are not produced by a chemical agent unless that agent or its metabolic breakdown products reach appropriate sites in the body at a concentration and for a length of time sufficient to produce a toxic manifestation.

The extensive range of health effects of trace element and heavy metal consumption has been illustrated throughout the literature. On a cellular level, it has been shown that a number of metallic ions cause metabolic disturbances in humans by upsetting production and function of certain enzymes, or cause a variety of other toxic effects (Momodu & Anyakore, 2010 within Rasheed et al., 2012). Other toxic effects may include the interaction between the heavy metal ion and specific target protein, resulting in a change of protein structure and function (Haddad, 2012). On a broader scale, Haddad (2012) expands on this by stating that metal deficiency diseases have become widely recognised, and pathological conditions arising from trace element excess have come to light. Certain essential trace elements are required in trace amounts for various physiological processes, but at higher concentrations, these micronutrients tend to be toxic and derange various physiological processes, thereby leading to diseases (Haddad, 2012). Micronutrients or microelements, as defined by Komorowicz et al. (2010) are small scale elements, whereas macroelements are large scale elements and are always found naturally in the environment. As such, the pattern discovered by analysis of the literature was that the health effects associated with the intake of higher concentrations of microelements were more serious than the consequences of an increased intake of the natural macroelements: sodium, potassium, calcium, magnesium, zinc and iron.

This conclusion is reinforced by the information in Table 10.5 of the 2011 Australian Drinking Water Guidelines (ADWG), entitled *Guideline values for physical and chemical characteristics.* The relevant information contained in the original document has been adapted and is displayed in Table 1-2 of Chapter One. Calcium, magnesium and potassium are not listed in this table, indicating that their presence in our drinking water poses little threat of adverse health effects, no matter their concentration. Similarly, there is no mention of cobalt, thallium, vanadium or thorium in the ADWG, and based on the literature, it can be presumed that if these elements were present in water, their concentration would be negligible. Iron, sodium and zinc have a guideline listed for aesthetic concerns only. In terms of health concerns, “Not necessary” is actually listed for sodium, while it is noted that there is “Insufficient data to set a guideline value based on health considerations” for iron and zinc (National Health and Medical Research Council,

2011), allowing the inference that any concentration of these metals in drinking water would not be great enough to warrant cause for health concerns.

The Australian Drinking Water Guidelines consider the observed health effects in humans in conjunction with the measurability of elements at low concentrations, as well as the lowest concentrations that are reasonably and economically achievable with current water treatment technologies (National Health and Medical Research Council, 2011). As a result, several elements had revised guideline values when compared with the previous version of the ADWG, released in 2004. Allowable health guideline concentrations increased from 0.007 to 0.01 mg/L for arsenic, and from 0.7 to 2 mg/L for barium. In addition, health guideline concentrations decreased from "Insufficient data to set a guideline value based on health considerations" to 0.06 mg/L for beryllium, and from 0.02 to 0.017 mg/L for uranium (National Health and Medical Research Council, 2011). All deviations from previous guidelines cited the consideration of more recent research that had become available since the previous ADWG were published.

For the majority of microelements of interest in this research, the literature analysed has verified that there is a fine line between beneficial and harmful amounts of these metals required by humans. Indeed, this evidence emphasises not only the need for a regulatory system such as the 2011 Australian Drinking Water Guidelines in Australia, but for testing to ensure adherence to these guidelines. The concentrations of trace elements and heavy metals as listed in the 2011 ADWG are very low, in parts per million (milligrams per litre) to parts per billion (micrograms per litre). Louie et al. (2012) recognise that the determination of trace elements to low detection limits in water samples is required to comply with drinking water guidelines and for the purpose of environmental monitoring by various regulating bodies. No individual parameter can express water quality sufficiently; water quality is normally assessed by measuring a broad range of parameters (Gazzaz et al., 2012). As a result, 26 trace elements and heavy metals are being tested in the course of this research. The method chosen to analyse the very low concentrations of these metals is Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). The reasons for choosing this technique are justified in the following section.

2.3 Inductively Coupled Plasma - Mass Spectrometry

Elements present in water are typically in the parts per billion to parts per million range, requiring the use of very sensitive analytical methodology (Komorowicz et al., 2010). Michalski et al. (2011) generally state that in the instance of environmental samples, when it is often necessary to determine trace concentrations of an analyte that occurs in a complex sample matrix or that may be subject to changes in pH and redox conditions, it is practical to use hyphenated techniques. Hyphenated techniques are based on the selective separation of the analyte ions and their determination with appropriate detectors (Michalski et al., 2011). Atomic spectroscopy is a principal tool of analytical chemistry and incorporates several hyphenated techniques.

Atomic spectroscopy techniques possess high sensitivity, the ability to distinguish one element from another in a complex sample and the ability to perform simultaneous multi-element analyses; additionally, many samples can be easily and automatically analysed in a timely manner (Harris, 2007). Becker (2005) agrees that atomic spectroscopy has become established with its ability to provide very sensitive, accurate, precise determinations of trace and ultratrace elements and species in liquid samples, including environmental materials and different types of water (rain, tap, river, sea or waste). Today, Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) is the most widely employed atomic spectroscopy technique out of Atomic Absorption Spectroscopy, Atomic Fluorescence Spectroscopy and Inductively Coupled Plasma-Optical Emission Spectrometry because of its high analytical sensitivity, as noted by Huang et al. (2011). The popularity and frequent use of this powerful technique is based on a fast, sensitive multi-elemental determination at very low concentrations for a wide variety of samples (Becker, 2005).

ICP-MS was developed by coupling an inductively coupled plasma source at ambient pressure with a vacuum-based quadrupole mass spectroscopy instrument by Gray and Date in 1975 (Becker, 2005). Becker (2005) explains that a liquid solution is nebulised in ICP-MS, and the fine aerosol formed is transported by argon to the ICP torch, where the plasma temperature is between 5000-8000K. The aqueous samples are evaporated, and the dissolved components are first vaporised into molecules, then dissociated into their constituent atoms and neutral elements, which are subsequently excited and ionised, all as

they transit through the high temperature plasma. This process is demonstrated in Figure 1-6 in Chapter One. An interesting advantage of ICP-MS is that the inductively coupled plasma works at atmospheric pressure, therefore reducing the time for trace analysis and opening up the possibility of many hyphenated techniques for liquids (Becker, 2005), including but not limited to FIA-ICP-MS, IC-ICP-MS and LC-ICP-MS. About 20 years after the introduction of ICP-MS, there are more than 5000 instruments are installed on the analytical market worldwide (Becker, 2005). In the eight years since this article's publication, it is safe to infer that the number of ICP-MS machines on the market has continued to increase, cementing ICP-MS as one of the most important analytical techniques in use today. Voica et al. (2012) confirm the importance of this method by observing that ICP-MS is available and adequate to identify and quantify metals present in natural and drinking waters at trace levels, a task of particular relevance for this research.

ICP-MS represents a considerable advance in sensitivity, accuracy and precision in trace element determination over previous atomic spectrometric techniques (Louie et al., 2012). Further reasons for increased use of ICP-MS are pointed out by Nunes et al. (2010), who identify advantages such as simultaneous multi-element measurement capability coupled with much lower detection limits. Additionally, ICP-MS offers a wider linear dynamic range, over nine decades of concentration range, allowing the determination of major and trace elements in the same sample (Parsons & Barbosa, 2007 in Nunes et al., 2010). Komorowicz et al. (2010) and Rasheed et al. (2012) both confirm the sensitivity of ICP-MS, reporting that very small concentrations of trace elements (below 0.1 µg/L) can be measured with high accuracy and repeatability. Despite its numerous advantages, the challenges associated with ICP-MS and the determination of trace elements in drinking water include low trace metal content and high matrix components (Rahman et al., 2012). Huang et al. (2011) agree with these authors, commenting that direct determination of some elements is often difficult due to a complex sample matrix and low concentrations of certain elements in water samples. Prior to direct analysis, a scan may be conducted on the water samples to determine which element concentrations are above the target water quality range (Greenfield et al., 2012). While an element scan is unnecessary for this research, the ability of ICP-MS instrumentation to perform such a task validates its position as one of today's most important analytical techniques.

Although the detection power of ICP-MS permits direct determination of trace metals at sub µg/L levels, interferences from polyatomic species arising from the major ions in the complex matrix of drinking water prevents a simple analysis (Rahman et al., 2012).

For example, interference is commonly expected between $^{40}Ar^{16}O^{+}$, a major background ion formed in ICP-MS analysis, and ^{56}Fe. Alternatively, ^{57}Fe, a minor isotope of iron, can be chosen instead, but this can be detrimental to the analytical sensitivity of this element. Isobaric interferences can also occur due to ions with similar mass. In this research, such interferences were checked for by measuring isotope ratios, and were then predicted and compensated for through the application of interference equations in the accompanying ICP-MS software. To minimise polyatomic interferences, Rahman et al. (2012) recommend the use of internal standardisation, high-purity reagents and nitric acid. The use of nitric acid is preferred over other mineral acids in almost all ICP-MS analyses, and this is further illustrated in section 2.3.1.

The determination of trace elements to low detection limits in water samples is required to comply with drinking water guidelines and, in some cases, for the purpose of environmental monitoring by various regulatory bodies (Louie et al., 2012). Cizdziel (2010) concisely summaries that ICP-MS has become a common method for monitoring environmental quality and processes, and for fingerprinting natural and anthropogenic pollution sources because of its multi-elemental capability, high sensitivity, low detection limits and ability to measure isotopes. ICP-MS can avoid the pitfalls of other atomic spectroscopy techniques, such as matrix effects, isobaric interferences, and instrumental drift, that can lead to poor data quality and misleading information (Cizdziel, 2010). Its extensive use is reported in the literature and these significant advantages therefore justify the use of ICP-MS in this research. It is an ideal analytical technique to simultaneously detect and identify various trace elements and heavy metals in environmental waters, including drinking waters. Despite the complex sample matrix of water, the collection and preservation of environmental samples for ICP-MS remains relatively simple.

2.3.1 Sample Collection and Preservation Processes

The attraction of analysing environmental samples with ICP-MS is its simplicity. The process of atomising a sample requires little sample preparation. In fact, for the methodology involved in this research, the preservation and preparation of a sample for analysis via ICP-MS incorporate the same procedural steps. There is a myriad of methods described within the literature, with many common approaches that will be analysed herein. Each method undertaken by all of these authors was developed and successfully applied to achieve their aims.

Authors Yabanli (2012), Voica et al. (2012), Damodhar and Reddy (2012), Said et al. (2012), Nirmal Kumar et al. (2012), Arslan (2012) and Krishna et al. (2009) all indicated that they used polyethylene terephthalate (PET) containers for the collection of water samples. Farooq et al. (2012) and Rasheed et al. (2012) are less specific, stating only that a plastic bottle or sample bottle was used, whereas Voica et al. (2012), Louie et al. (2012), Reddy et al. (2012), Grellier et al. (2012) and Ayoko et al. (2007) specifically note that high density polyethylene containers were used. High density polyethylene (or HDPE) containers are proven to be free from trace element contamination (Louie et al., 2012) and are therefore the most ideal container for use in this research. Alternatively, Teflon bottles are identified by Komorowicz et al. (2010) as appropriate water collection containers.

In many cases, the containers used to collect water samples were previously washed or soaked in a nitric acid solution for an extended period of time, usually at least 24 hours (Damodhar & Reddy, 2012). Upon collection of the water samples, Damodhar and Reddy (2012) rinsed each container with the sample water three times before completely filling the container. Similarly, Said et al. (2012) rinsed their acid-washed PET collection containers with distilled water prior to filling them with sample water. Adiana et al. (2011) exceeded the norm so far seen in the literature by soaking all labwares to be used in the course of sample collection and preparation in diluted nitric acid and performing all works under a laminar flow hood to avoid contamination.

In the literature analysed, the majority of water samples collected were raw water samples from lakes and rivers, or water treatment facilities. Because of this, many authors describe a simple filtration process. Damodhar and Reddy (2012) state the use of a Whatman glass microfiber filter, while Rasheed et al. (2012) illustrate the use of Whatman No. 1 filter paper. In addition, 0.45 µm membrane filters were used by Said et al. (2012), Singh et al. (2012) and Arslan (2012). Reddy et al. (2012) plainly state that filtered samples were directly introduced to the ICP-MS, and others simply indicate that field filtration preservation techniques were used (Rahman et al., 2012). Although the water samples collected throughout this research are of drinking water quality, filtration is still deemed a necessary step due to the sensitivity of the ICP-MS instrumentation.

Following the careful collection and optional filtration of samples for analysis, all authors were unanimous in the action of acidifying and refrigerating the water samples for preservation. In the event of acidification, all authors used nitric acid. The Australian and International Standards recommend the use of nitric acid for the preservation of trace

elements in ICP-MS determination (Louie et al., 2012). Voica et al. (2012) suggest that the use of nitric acid stabilises the water sample. Some authors acidified their samples to specific pH levels, namely pH levels no greater than 2, such as Yabanli (2012), Damodhar and Reddy (2012), Said et al. (2012), Krishna et al. (2009) and Grellier et al. (2012). Louie et al. (2012) confirm that three of the most preferred methods for ICP-MS determination of multi-elements recommend the addition of nitric acid until the pH of the water sample is no greater than pH 2.0. Jiang et al. (2012) and Rahman et al. (2012) also agree that high-purity reagents, for example ultrapure nitric acid and Milli-Q water, are to be used for sample preparation due to the high sensitivity of ICP-MS. The standards used in sequence with the water samples to be analysed should also be high-quality reagents. The variety of standards used in the literature analysed here include multi-element calibration standards, blank samples, spiked samples and internal standards, all of which are standard and/or certified reference materials. Nirmal Kumar et al. (2012) summarise that data quality is ensured through careful standardisation, blank measurements, spike and duplicate (or triplicate) samples.

Finally, all samples and standards prepared are refrigerated for preservation. Damodhar and Reddy (2012), Said et al. (2012), Nirmal Kumar et al. (2012), Arslan (2012), Adiana et al. (2011), Grellier et al. (2012), Ayoko et al. (2007), De Luca et al. (2008), Komorowicz et al. (2010) and Huang et al. (2011) all specify refrigeration at $4^{o}C$ prior to analysis by ICP-MS. In addition, De Luca et al. (2008) also ensured their water samples were tested within 48 hours for maximum accuracy. Feldman (1974) within Louie et al. (2012) had reported significant loss of mercury in nitric acid in both HDPE and glass containers within 10 days. This loss of such an interesting element is a confirmation of the need for a prompt analysis of water samples in addition to preservation efforts made. Based on the findings from the analysis of the literature, the method employed for this research will include the collection, filtration, acidification and refrigeration of water samples, with analysis to be conducted as soon as reasonable. The results achieved through the analysis performed by ICP-MS will be compared to the current 2011 Australian Drinking Water Guidelines and will be further investigated by using a series of chemometric techniques.

2.4 Chemometrics

A large amount of data will be produced through the analysis of 26 trace elements and heavy metals of interest via Inductively Coupled Plasma – Mass Spectrometry. The generation of these data therefore requires meaningful presentation to ensure that they are understandable and accessible to various groups including planners and decision makers, and the general public (Gazzaz et al., 2012). Ayoko et al. (2004) believe it is not enough to list or tabulate the concentrations of different contaminants or the characteristics of variables, but that a method or methods need to be applied so as to allow for quantitative assessment and objective comparisons. To address this issue, many recent studies have combined elemental analysis results with multiple statistical techniques that utilise chemometric principles to achieve a deeper understanding of information available in the data (Bong et al., 2013). Chemometrics encompasses advanced statistical techniques specific to scientific applications. Here, a thorough analysis of the chemometric techniques used throughout the literature will provide the basis of the statistical methodology applied in this research.

Chemometrics is a term that was first proposed in 1972 to describe the chemical field focused on the application of mathematical, computational and logic methods to maximise the extraction of information from data and experimental measurements (Kokot & Ayoko, 2005; Kokot et al., 1998). Haswell (1992) similarly states that chemometrics is the combination of mathematical, statistical and other logic-based methods to efficiently manage and interpret chemically derived data (Arumugam et al., 2012). Over the last few decades, chemometrics has become a recognised form of analytical chemistry. Chemometrics has been widely used, specifically in environmental science, and is supported by extensive literature. It can be applied to solve problems containing both quantitative and qualitative information. Chemometrics involves the acquisition and subsequent extraction of valuable information from data. It can be used in pattern recognition, classification, discriminant analysis, calibration, prediction and multi-criteria decision making methods (MCDM). The advantages of employing chemometrics in analytical chemistry are that results are systematic, reproducible and amenable to visual display. There are a multitude of ways chemometrics can be used to make the most of any data acquired; however, Kokot et al. (1998) firmly state that chemometrics cannot fix poor sampling, calibration or validation, nor does it replace good analytical laboratory practice.

Pre-treatment of the data is a very important step prior to the application of any chemometric technique, and is often not fully addressed in the literature. Wu et al. (2012) imply that few studies have considered appropriate data pre-treatment methods, such as estimation of missing data, examination of normal distributions, and data transformation, all of which can greatly influence the results of a multivariate analysis. Additionally, the selection of variables is very important. The amount of relevant information does not necessarily increase when a higher number of variables are included. On the contrary, it could increase random noise (De Luca et al., 2008 in Wu et al. 2012). Liu et al. (2009) note that any chemometric application begins with a data matrix. For example, data matrices obtained in this research will list water samples from different sites as objects in rows, and the trace elements and heavy metals of interest as variables in columns.

A data matrix is generally pre-treated so as to prepare the data for chemometric analysis, via mean centring, standardisation or normalisation, in order to make objective comparisons (Liu et al., 2009). As exampled by these authors, there are numerous pre-treatment methods employable. De Luca et al. (2008) comment that the normalisation process they used was necessary to obtain comparable data as the parameters of their research were all presented in different units of measurement. Mladenovic-Ranisavljevic et al. (2012) note that not all parameters have the same impact on water quality, and this is taken into account by many authors. Farooq et al. (2012) used normalised data, Fu and Wei (2012) standardised their samples in order to classify them, Krishna et al. (2009) and Wang et al. (2012) standardised their data through z-scale transformation (otherwise known as auto-scaling), with the latter explaining that this was done in order to avoid misclassification due to the wide differences in data dimensionality. Additionally, Singh et al. (2012) state that multivariate statistical methods require data to be normally distributed. However, the data set obtained by these authors had higher than desirable skewness, requiring further treatment to log transform the entire data set in order to significantly reduce the skewness in all variables. Z-scale transformation was then also carried out for Cluster Analysis (Singh et al., 2012).

Prior to any data pre-treatment, descriptive statistics of the original data are found to determine basic information, correlations and distributions. Descriptive statistics include the size of the data set, the number of missing variables, mean and geometric mean, standard deviation, standard error, minimum and maximum values, and the subsequent range, the confidence interval of the mean, and the skewness of the data, to name a few. In some cases, descriptive statistics are visualised through the use of box plots, as in Kumar

et al. (2012). Basic techniques like an Analysis of Variance (ANOVA), which is used to test the hypothesis that the means of two or more groups are not significantly different, have been used by Damodhar and Reddy (2012), Muduli et al. (2012), Fu and Wei (2012) and Kumari et al. (2012). Komorowicz et al. (2010) performed ANOVA in order to isolate existing differences in element concentration between particular sampling stations. These authors also performed a second ANOVA to show the differences in concentration of given elements depending on season, which revealed considerable differences for many elements (Komorowicz et al., 2010). Similarly, the Pearson Correlations Coefficient method – a measure of the strength of linear dependence between two variables, or the Spearman Rank Correlation method – a non-parametric measure of statistical dependence between two variables, were applied by Jiang et al. (2012), Fu and Wei (2012), Kumari (2012), and Arumugam et al. (2012), or Wang et al. (2012), Singh et al. (2012) and Grellier et al. (2012), respectively.

The chemistry of water is characterised by complex correlations and interactions among a wide range of variables (Singh et al., 2012). Sajdak and Pieszko (2012) illustrate that despite this complexity, most chemometric methods can be used to analyse data on water pollution. Of the wide variety of chemometric techniques available, Principal Component Analysis (PCA) and Cluster Analysis (CA) are the most extensively used and are often used in conjunction with one another. In research by Farooq et al. (2012), PCA and CA were used to evaluate similarities and dissimilarities among sampling sites, to expose the group structure of samples, to gauge variation and to identify water quality variables responsible for variation in river water quality. Sajdak and Pieszko (2012) also used PCA and CA during testing, and described them as very effective techniques for finding relationships between variables. PCA is aimed at finding and interpreting hidden complex and casually determined relationships between features in a data set (Arumugam et al., 2012). Vieira et al. (2012) acknowledge that the multivariate techniques, PCA and CA, lead to a better understanding of the water quality and the ecological status of studied systems. These authors add that these statistical methods can be used as classification methods, grouping the water pollutants according to their sources (Vieira et al., 2012).

Kumar et al. (2012) observes that PCA is one of the best statistical techniques for extracting linear relationships among a set of variables. Pinto et al. (2012) add that PCA has gained more acceptance over other techniques due to its ability to handle large data sets and reduce dimensionality to a manageable size while keeping as much of the original information as possible. PCA enables the variance in the data to be accounted for as

concisely as possible and identifies the most important variables in the data (Singh et al., 2012). A complete and more technical understanding of PCA is provided by Arslan (2012), who states that the PCA technique extracts the eigenvalues and eigenvectors from the covariance matrix of original variables. It allows the discovery of association between variables, thus reducing the dimensionality of the data set. The Principal Components (PCs) are the uncorrelated orthogonal variables obtained by multiplying the original correlated variables with the eigenvector, otherwise known as the loadings or weightings. The eigenvalues of the PCs are the measure of their associated variance, the participation of the original variables in the PCs is given by the loadings and the individual transformed observations are called scores (Arslan, 2012). It is generally said that the first few PCs explain the majority of the variance within the original data set, the first one accounts for the most variance, and each PC afterwards counts for progressively less variance (Arslan, 2012). Xu et al. (2012) simply summarise that PCA is a technique that reduces the original variables to minority underlying factors or principal components, which account for as much of the original variance as possible. These authors continue, saying that PCA and CA methods have great application potential for better management of water quality monitoring systems (Xu et al., 2012).

The overall aim of cluster analysis is to achieve a set of clusters in which the objects included in the same cluster are similar to each other and different from the other objects belonging to other clusters (Manly, 1994 within Vieira et al., 2012). CA is an unsupervised pattern recognition technique, designed to detect hidden groups in a set of objects, so that the members of each cluster behave similarly to each other and the groups are maximally separated (Xu et al., 2012). CA has the ability to discover intrinsic structures or an underlying behaviour of a data set without making any previous assumption regarding the data, as well as the ability to separate the objects into categories or clusters based on their similarities (Xu et al., 2012). Kumari et al. (2012) infer that CA is considered a better approach than other techniques such as PCA because it identifies the underlying factor in data without the need for any pre-assumption or a null hypothesis, and no simplification of data is required. Research by Yang and Liu (2012) prominently features cluster analysis, in addition to a large number of studies that have used this technique to successfully classify water samples through comparisons based on multiple parameters from different samples (Arslan, 2012).

The variations in Cluster Analysis include k-means clustering, fuzzy clustering and hierarchical clustering. The k-means clustering uses Euclidean distance for partitioning

corresponding to the mean of each cluster. The k-means method is considered one of the simplest and most classical methods for data clustering, and this simplicity makes it one of the most widely used methods in practical implementations (Aggarwal & Reddy, 2014). Fuzzy clustering, examined in detail at a later point, deals with uncertainty and vagueness, and can be useful in the environmental field where data is often not fully available (Cabanillas et al., 2012). Hierarchical clustering techniques are perhaps the most popular of all of the cluster methods, and the literature surrounding them is enormous (Everitt, 1980). Hierarchical Cluster Analysis (HCA) is the method employed in this research, and is a non-parametric, unsupervised pattern recognition technique that does not depend on assumptions of normality (Pinto et al., 2012). Resulting clusters of objects in HCA exhibit high internal homogeneity and high external heterogeneity (Arumugam et al., 2012). HCA is represented through dendrograms, or tree diagrams, where the number of clusters may be indicated graphically (Xu et al., 2012). The use of dendrograms is demonstrated by Farooq et al. (2012), Muduli et al. (2012) and Sajdak and Pieszko (2012).

Kumari et al. (2012) describe cluster analysis as an appropriate tool for the interpretation of several related water quality parameters and observe that it has been used for the evaluation of temporal and spatial variations in such water quality parameters.
Xu et al. (2012) observe that studies conducted prior to their own have confirmed that PCA and CA methods could supplement each other and that a combination of the two approaches would be suitable for analysing and resolving environmental problems. These authors stated that PCA and CA methods had great application potential for better management of water quality monitoring systems (Xu et al., 2012). Singh et al. (2012) concluded that multivariate techniques have led to a better understanding of the roles of correlated and interdependent variables. These analyses have also provided insight into the underlying structure of the data set which is not otherwise apparent.

In addition to PCA and CA, techniques such as Factor Analysis (FA), Discriminant Analysis (DA) and Trend Analysis (TA) can assist in identifying the most important variables influencing quality aspects and can lead to a better understanding of variable interactions as well as temporal and spatial variations (Singh et al., 2012). CA, FA and PCA have been widely used as unbiased methods in analysis of water quality for drawing meaningful information (Arslan, 2012). Singh et al. (2012) note that FA performed after PCA can further refine the data by reducing the contribution of less important variables. The main distinction between PCA and FA is that PCA examines the variance in each of the variables, while FA considers the variance in the data as a whole. Additionally, the combined use of

PCA and FA can bring to fore latent but important variables (Singh et al., 2012). Exampled in research by Arslan (2012), FA has been applied to obtain correlations among the constituents of groundwater samples. Krishna, Satyanarayanan and Govil (2009) also used FA in their multivariate analysis, and agree with Singh et al. (2012) and Wang et al. (2012), by confirming that FA does indeed further reduce the contribution of less significant variables obtained from PCA, and the new group of variables, or varifactors, are extracted by rotating the axis (with varimax rotation or other available methods) defined by PCA. A varifactor can include unobservable, hypothetical latent variables, while a principal component is a linear combination of observable water quality variables (Krishna et al., 2009).

In addition, Trend Analysis (TA) is described by Pinto et al. (2012) as an exploratory data visualisation technique useful in identifying emerging patterns of historic water quality data records. These authors applied a combination of Factor Analysis, Heirarchical Agglomerative Cluster Analysis (HACA) and Trend Analysis to aid in the evaluation of long term historic data sets (Pinto et al., 2012). Finally, Discriminant Analysis (DA) is a linear, parametric technique and one of the most common approaches to classification. DA focuses on identifying optimal boundaries between groups. Discriminant Analysis was used in research performed by Bong et al. (2012), and Singh et al. (2012) suggest its use in understanding interactions between variables and identifying the most important variables.

Another interesting chemometric technique is fuzzy clustering. Cabanillas et al. (2012) describe fuzzy clustering as a well known theory applied to deal with uncertainty and vagueness. It is especially useful in the environmental field where data are often not fully available (Cabanillas et al., 2012). McKone and Deshpande (2005) state that the key advantage of fuzzy clustering methods is how they reflect the human mind in its remarkable ability to store and to process information that is consistently imprecise, uncertain and resistant to a classification. Fuzzy clustering relies on fuzzy logic in its implementation. Classically, it is assumed that a fact is either true or not true, whereas fuzzy logic implies that a fact is never totally true or totally false, instead that it will be true or false with a certain degree of membership (Cabanillas et al., 2012). The fuzzy logic method allows soft and hard classifications. Soft classification acknowledges that objects in one class can have properties in common to objects in other classes; that is to say that these objects are fuzzy. Hard classification forces objects into their most preferred class and presupposes that there are only specific classes with no overlap. The fuzzy nature of this method dictates its frequent use in partnership with at least one other method.

Previous research by Liu et al. (2009) demonstrated the application of fuzzy clustering for the analysis of water quality data in combination with multicriteria decision making methods, the most popular of which is PROMETHEE and GAIA.

Qualitative non-parametric ranking methods such as PROMETHEE (Preference Ranking Organisation METHod for Enrichment Evaluations) and GAIA (Graphical Analysis for Interactive Assistance) can facilitate the ordering of a number of objects (i.e. water sources) according to preference and weighting conditions that have been pre-selected by the user and are applied to variables (i.e. heavy metal concentrations) (Ayoko et al., 2007). PROMETHEE and GAIA have been effectively applied to various problems in analytical, environmental and engineering chemistries (Liu et al., 2009). Environment management is considered the most popular topic in PROMETHEE applications and a large amount of literature related to this topic can be found (Behzadian et al., 2010). This multicriteria decision making (MCDM) method is considered the most popular qualitative approach in chemometrics. Ayoko et al. (2007) report that GAIA uses PCA techniques to evaluate and display PROMETHEE results visually. An advantage of GAIA procedures over other multivariate data analysis methods is that reduction and standardisation of data to unit variance is unnecessary, since PROMETHEE serves as a data pre-treatment procedure (Ayoko et al., 2007). The main advantage of PROMETHEE, as stated in an earlier article by Ayoko et al. (2003), is that as a non-parametric multivariate ranking procedure, it is applicable to a data matrix consisting of just a few samples. There are two types of ranking outcomes achievable with PROMETHEE. PROMETHEE I is a partial ranking order and can have three possible outcomes, where one object is preferred to another, there is no difference between the two objects or the objects cannot be compared (Ayoko et al., 2003). Alternatively, PROMETHEE II is a complete ranking order wherein objects can be forced into order. Although PROMETHEE II appears to be more efficient in ranking objects, it is less informative than PROMETHEE I which is usually considered better, as a partial ranking is closer to the truth (Ayoko et al., 2004).

In a study performed by Mladenovic-Ranisavljevic et al. (2012), PROMETHEE and GAIA were applied in order to perform the ranking of measuring points based on multiple criteria simultaneously, in terms of ten water quality parameters. These authors justify their use of this multicriteria decision making method on the basis of its widespread application in the analysis of environmental pollution problems. PROMETHEE performed a complete ranking from best to worst location based on the presence of harmful water quality parameters in the river. In defining weight criteria, Mladenovic-Ranisavljevic et al. (2012) take into

account the fact that not all parameters have the same impact on water quality. Then, dimensionless axes are used for segmentation of space in order to better present the strengths of the actions and criterions according to their position in the GAIA plane, positions also relevant to the *pi* decision axis (Mladenovic-Ranisavljevic et al., 2012). Such MCDM methods are powerful tools that can provide guidance for many practical problems where there are many stakeholders, and they offer extensive opportunities to extract compromise solutions which take into consideration not only the rational findings of science and technology, but also ethics and subjectivity of the decision maker (Kokot & Ayoko, 2005).

De Luca et al. (2008) state that multivariate procedures have been proven suitable for environmental quality assessment. Multivariate techniques were further investigated by De Luca et al. (2008) for the principal advantage of analysing a very high number of data and building a multivariate model with the ability to predict new unknown samples. Partial Least Squares (PLS) is a chemometric technique widely used to develop predictive models and is the most commonly used form of multivariate calibration. PLS works with two matrices, *X* (e.g. factors or independent variables) and *Y* (e.g. responses or dependent variables) (Ayoko et al., 2007). In contrast, PCA models variance using only independent variables (*X*). PLS attempts to find the least complex model that explains the data by relating *X* and *Y* to each other through regression. The main objectives of this technique are to well approximate *X* and *Y*, and to model the relationship between them (Ayoko et al., 2007). PLS models always undergo a validation process, and this is done internally as cross-validation.

In 1978, Wold detailed cross-validation as involving keeping out parts of the data during model development, developing the model from reduced data, predicting the parts kept out by different models and comparing the predicted values with actual values (within Ayoko et al., 2007). Alternatively, validation can be performed externally by splitting the entire data matrix into two equal halves, where one half is used as the calibration set and the other as the prediction set (Ayoko et al., 2007). Results achieved by Ayoko et al. (2007) support the viability of the proposed concept of using multivariate data analysis methods to predict water quality from a few easily measured variables. The most important variables influencing water quality previously identified from PCA plots were subsequently used in PLS analysis for modelling and predicting the levels of other water pollutants (Ayoko et al., 2007). De Luca et al. (2008) emphasise the care with which the calibration set should be selected, as excluding important variables at this stage may lead to misleading results when

building a model. Application of this chemometric technique offers a reliable and better understanding of the hydrochemistry and hydro-chemical processes in the area of interest (De Luca et al., 2008).

There exists a vast arsenal of chemometric techniques employable to process large data sets. The literature analysed here is by no means an exhaustive list of available techniques. Other such methods can include nearest neighbour classification methods, class analysis through SIMCA (Soft Independent Modelling of Class Analysis), KMO (Kaier-Meyer-Olkin) measure of sampling adequacy (Arumugam et al., 2012; Wang et al., 2012) and even artificial neural networks (ANN), used by Gazzaz et al. (2012) for its potential to produce models capable of efficient forecasting of water quality with reduced computation time and possible errors. Applications of ANN to environmental problems are becoming more common (references within Khan et al., 2012). For example, Khan et al. (2012) use principal component scores of numerous water quality parameters as input variables in ANN models for predicting water quality in the Langat River Basin in Malaysia.

In this research, chemometric analysis will be used as another experimental platform in addition to the analyses performed by ICP-MS. In the application of chemometric techniques, objectivity is key. The minimisation of subjectivity and facilitation of method transparency means that the role of the decision maker is minimised (Kokot & Ayoko, 2005). As a result of minimising a decision makers' influence upon the employment of a method, the results achieved can be considered unbiased and consequently, can confidently be put into practice. Kokot and Ayoko (2005) suggest that it is useful to apply more than one method to find the best solution to the problem, advice that will be followed in the course of this research to ensure thorough analysis and to produce the maximum amount of information. Batista et al. (2012) summarise that the patterns arrived at by these systems are transformed into knowledge in order to make decisions. Ultimately, a predictive model will be created for the purpose of water quality testing worldwide. This approach is illustrated by Ayoko et al. (2007) who confirm that the globalisation of information with the use of chemometrics is a very feasible approach for studying prediction and performance issues in water quality.

2.5 Implications

The thorough analysis of the literature, encompassing the four main themes of water, toxicology, ICP-MS and chemometrics, provides the theoretical framework for this research, as well as demonstrating the gaps in the knowledge that this research seeks to fulfil. The literature regarding water quality and quantity clearly demonstrate the need for ongoing assessment of both raw and potable water for environmental and health reasons. Additionally, the presence of trace elements and heavy metals in all waters is acknowledged, and these elements are investigated as lithogenic and anthropogenic contaminants that may be essential or toxic to human health. Extensive literature validates the use of ICP-MS in the analysis of environmental samples, including water, to extremely low concentrations; and almost all authors cited were unanimous in sample collection and preservation methodologies. The plethora of chemometric techniques available can be effectively applied to a multitude of scenarios, as proven in the literature analysed.

There has been extensive investigation into trace element and heavy metal contaminants in natural water bodies such as lakes and rivers; however, there is a significant lack of investigation into such contaminants in potable water, especially locally. In order to fulfil this gap, this research will predominantly analyse potable water samples of tap, tank, filtered and bottled water. Additionally, raw and treated water samples will be collected. This approach is similar to Rahman et al. (2012), who stated that their samples were taken from treatment plants, resulting in a total of four treated, four pre-treated and four raw water samples collected for the analysis. Similarly, the 2011 ADWG suggest that sampling should include the raw water source, in this case, the Brisbane River and its tributaries; water entering the distribution system after disinfection or clarification, otherwise known as treated water; water at a variety of points throughout the distribution system and finally, at the consumers' tap. Given the scope and time constraints of the research, the aim is to analyse raw water sources from selected dams, lakes, rivers and creeks, samples of treated water from Mt Crosby West Bank WTP, mains water collected from throughout the distribution system, and finally, potable water samples from houses in the greater Brisbane area. The analysis of such a variety of water samples will enable the determination of trace elements and heavy metals in each water source, and will also bring to light the existence of any anthropogenic influences in South East Queensland's water supply system.

The discrimination of trace elements and heavy metals present in each water source will also lead to source fingerprinting. Just as Singh et al. (2012) succeeded in identifying natural associations among groundwater sampling sites and variables, this research aims to identify the relationships between water sources, and associations among the variables, that is, the trace elements and heavy metals, in different sources of water.

The analysis and fingerprinting of the variety of water samples will be accomplished through the combined use of ICP-MS and chemometrics, whereby numerous chemometric techniques will be utilised to extract the maximum amount of information from the data. It is believed that there remains a gap in understanding the results of various environmental analyses, a gap that can be filled through the application of chemometrics.

Historical data collected from 2008 to 2012 will be analysed in addition to current data from sample collection in 2013 in an attempt to compare and contrast the climatic extremes of drought and flood experienced in South East Queensland. Such an analysis of the possible effects of climatic extremes on the heavy metal content in water has not been undertaken in the literature analysed and will be thoroughly researched.

As a result of the information examined in this critical review of the literature, the hypothesis for this research is that quantitative ICP-MS data modelled through the use of chemometrics will allow factors including water sources, sources of contaminants and effects of changing climatic conditions to be identified from trace element and heavy metal content of potable Brisbane water.

Chapter Three: Research Design and Methodology

3.1 Introduction

This chapter introduces the methodology designed and used to investigate the gap in the research outlined in Chapter Two. The following sections will detail the range of methodologies used to answer the proposed research questions and as a result, fulfil the existing knowledge gaps through original contributions to this research area. This research is methodologically diverse, incorporating qualitative, quantitative and statistical methods. All methods used are described in depth with the view to be replicated in future research. This will be accomplished by detailing each methodology, the setting and participants of the research, and the materials, samples, instruments and procedures used to achieve the results. These methodologies converge in this chapter to fulfil the hypothesis for this evidence-based research.

3.1.1 Research Problem

Research conducted by authors such as Gazzaz et al. (2012), Louie et al. (2012), Greenfield et al. (2012), Yabanli and references within Yabanli (2012) has made it clear that the concentration of trace elements and heavy metals is a vital aspect of water quality. There have been numerous investigations worldwide into the presence and cause of heavy metal contamination, yet very few if any of the studies analysed in Chapter Two: Literature Review examine their presence in potable water. As previously demonstrated in sections 2.1 and 2.2 of Chapter Two and specifically by De Luca et al. (2008), Ayoko et al. (2007), Voica et al. (2012), Vieira et al. (2012), Pinto et al. (2012) and Haddad (2012), it is important to understand the general factors influencing raw water quality: natural, agricultural, industrial, microbial and anthropogenic contaminants. Understanding the impact of these contaminants on raw waters is necessary because the raw water from Brisbane River and its tributaries is treated for consumption and use throughout the greater Brisbane area.

The existing gap in the knowledge to be fulfilled encompasses the concentrations of trace elements and heavy metals in potable water by the time this water reaches the consumers' taps. This gap is the result of a number of additional factors that have not yet been considered, including the source of raw water and distribution of treated water, the components of the water delivery system (i.e. composition of mains and household pipes) and the possible effect of climatic extremes (drought and flood) on the heavy metal content of the water.

Therefore, the hypothesis for this research is that quantitative ICP-MS data modelled through the use of chemometrics will allow factors including water sources, sources of contaminants and effects of changing climatic conditions to be identified from trace element and heavy metal content of potable Brisbane water.

The aim of this research and the questions and objectives designed to accomplish this aim are detailed in the following sections. Additionally, each objective is broken down using a flow diagram, so that the various methodologies applied in fulfilling these objectives can be seen.

3.1.2 Research Aim

The aim of this research is to investigate the concentration of trace elements and heavy metals in a variety of water sources from the greater Brisbane area. The combined use of Inductively Coupled Plasma – Mass Spectrometry and chemometrics will provide a deeper analysis and understanding of the variability in trace elements, all of which have been selected for their effect on human health, as well as their aesthetic nature in palatable potable water. The overall aim of this research is to: identify different water sources, i.e. potable waters, raw water, treated water and mains water, and probable sources of trace element and heavy metal contamination in each of these sources, compare the data with the 2011 Australian Drinking Water Guidelines (ADWG), establish if changing climatic conditions have an effect on potable water quality, and develop a predictive model for water quality based on the concentrations of metal ions present in all six years of data analysed in this research.

3.1.3 Research Questions

The questions designed to accomplish the research aim are as follows:

I. Can the heavy metal fingerprints of various water sources be distinguished?
   a. Is raw water easily distinguishable from treated water?
   b. Do the trace element and heavy metal concentrations in treated water change by the time it reaches our taps?
   c. Can different potable water sources (i.e. tap water, filtered water, bottled water, tank water) be distinguished by chemometric analysis of their trace element and heavy metal concentrations?
   d. Can the source of the water be determined from its trace metal profile?

II. Do changing climatic conditions affect potable water quality?

III. Which chemometric techniques can best maximise the elucidation of information collected from the data?

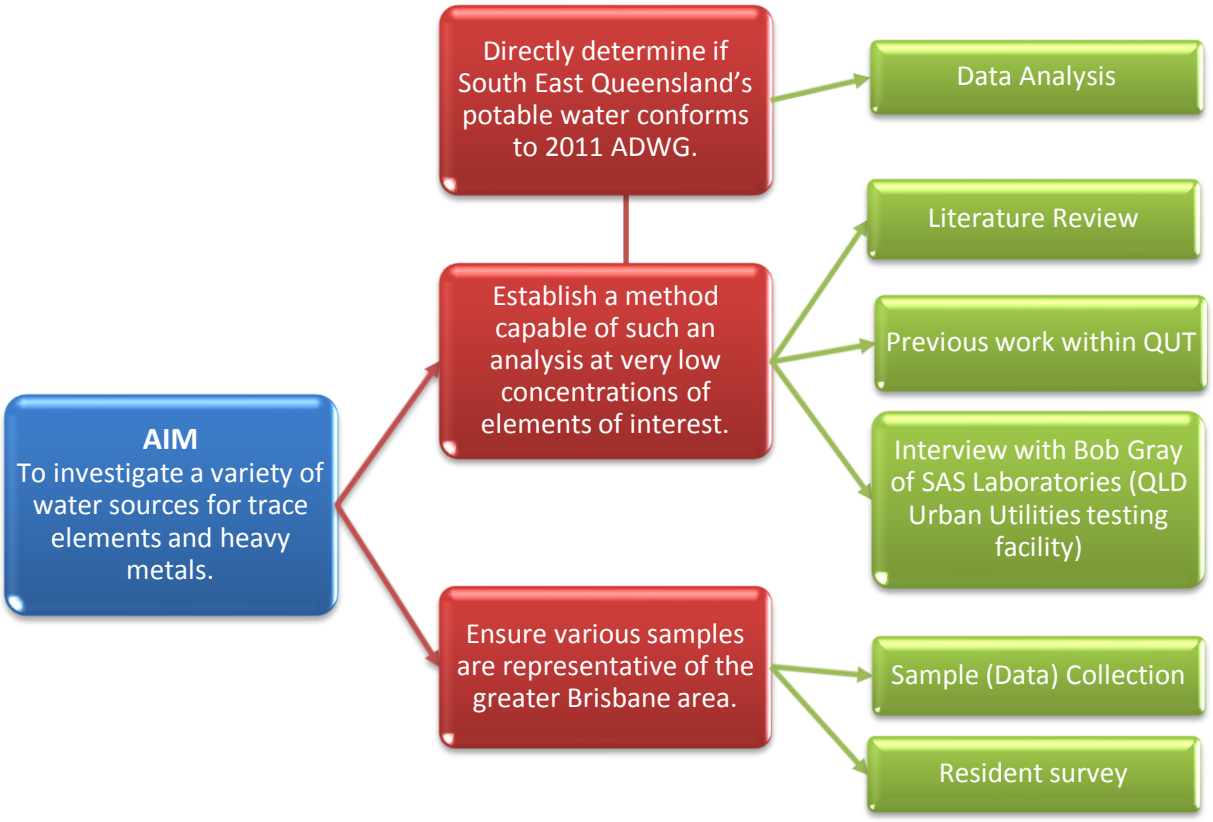
IV. Can metal ions be predictors for water quality?

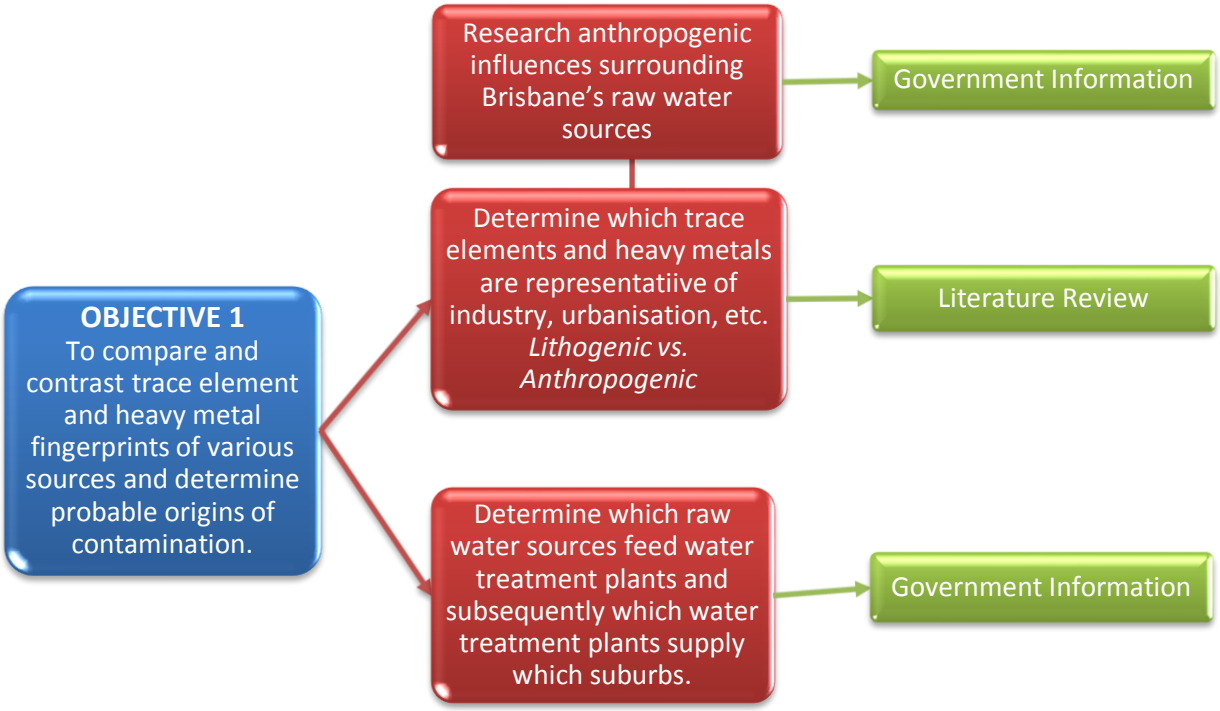
3.1.4 Research Objectives

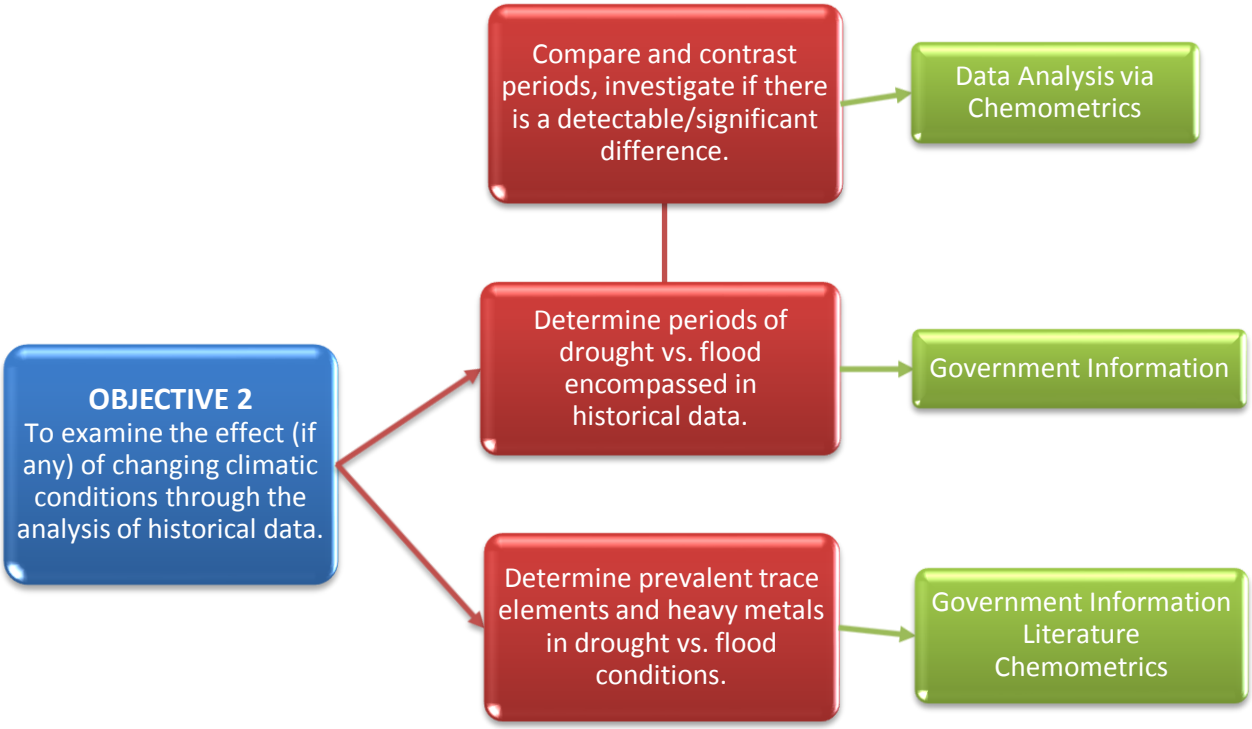
The following research objectives are formulated to answer the above research questions and consequently the research aim. The objectives are to:

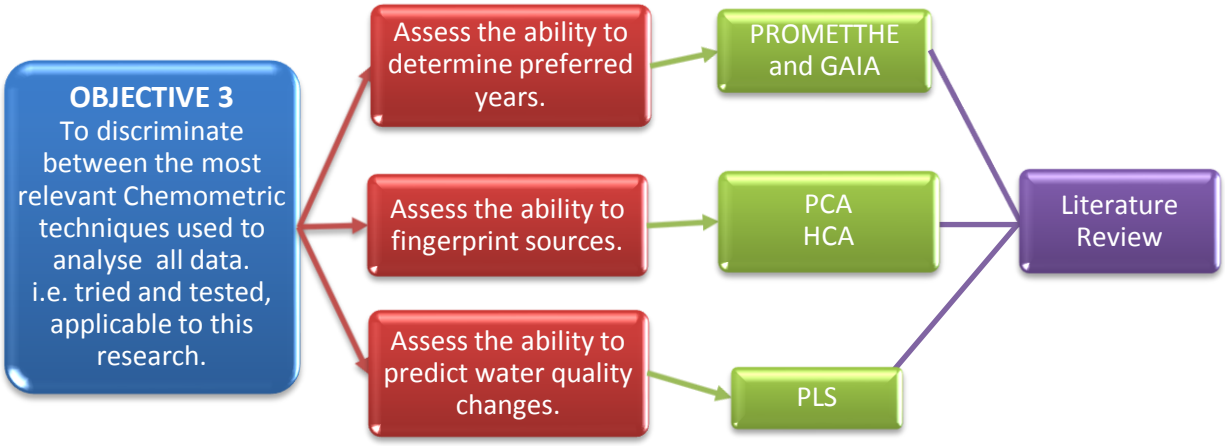
- Compare and contrast the trace element and heavy metal fingerprints of the various sources and determine probable origins of contamination.
- Examine the effect (if any) of changes in climatic conditions through the analysis of historical data.
- Discriminate between the most relevant chemometric techniques used to analyse all data to determine usefulness.
- Establish if metal ions can be predictors for water quality through model development.

The diagrams in Figure 3-1 demonstrate the flow of each objective and outline the tools used to fulfil these research objectives.


AIM
To investigate a variety of water sources for trace elements and heavy metals.
Directly determine if South East Queensland's potable water conforms to 2011 ADWG.
Data Analysis
Establish a method capable of such an analysis at very low concentrations of elements of interest.
Literature Review
Previous work within QUT
Interview with Bob Gray of SAS Laboratories (QLD Urban Utilities testing facility)
Ensure various samples are representative of the greater Brisbane area.
Sample (Data) Collection
Resident survey


OBJECTIVE 1
To compare and contrast trace element and heavy metal fingerprints of various sources and determine probable origins of contamination.
Research anthropogenic influences surrounding Brisbane's raw water sources
Government Information
Determine which trace elements and heavy metals are representatiive of industry, urbanisation, etc. *Lithogenic vs. Anthropogenic*
Literature Review
Determine which raw water sources feed water treatment plants and subsequently which water treatment plants supply which suburbs.
Government Information


OBJECTIVE 2
To examine the effect (if any) of changing climatic conditions through the analysis of historical data.
Compare and contrast periods, investigate if there is a detectable/significant difference.
Data Analysis via Chemometrics
Determine periods of drought vs. flood encompassed in historical data.
Government Information
Determine prevalent trace elements and heavy metals in drought vs. flood conditions.
Government Information
Literature
Chemometrics


OBJECTIVE 3
To discriminate between the most relevant Chemometric techniques used to analyse all data.
i.e. tried and tested, applicable to this research.
Assess the ability to determine preferred years.
PROMETTHE and GAIA
Assess the ability to fingerprint sources.
PCA
HCA
Assess the ability to predict water quality changes.
PLS
Literature Review

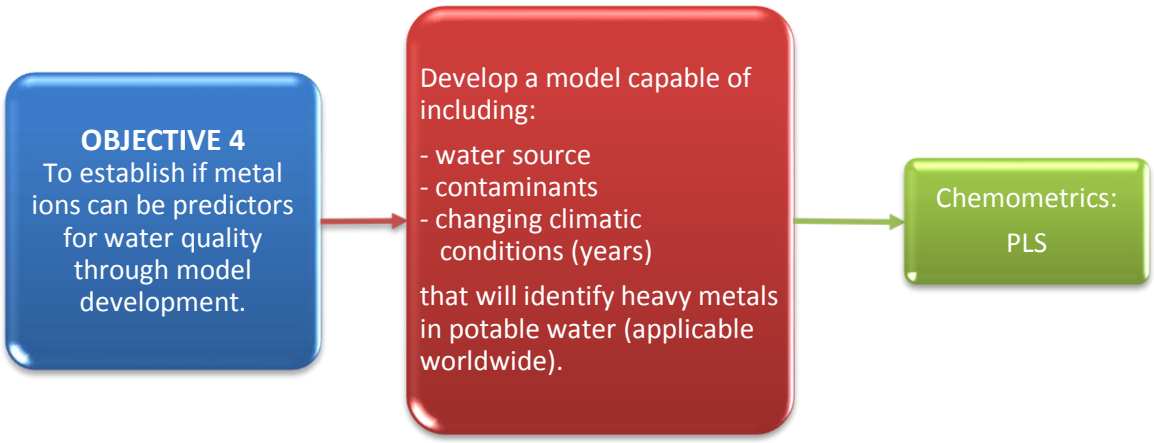


Figure 3-1. Research aim and objective flow diagrams.

The culmination of the research aim, questions and objectives is the overall hypothesis for this research: that quantitative ICP-MS data modelled through the use of chemometrics will allow factors including water sources, sources of contaminants and effects of changing climatic conditions to be identified from trace element and heavy metal content of potable Brisbane water.

3.2 Methodology

The underpinning methodologies used to achieve the research aim and objectives are diverse, involving the use of quantitative, qualitative and statistical methods. The development of these methodologies was aided by the extensive literature review, course work undertaken and background knowledge. Each methodology is a vital approach to answering the proposed research questions. All of these methodologies are intertwined throughout the research and are illustrated in the following sections.

3.2.1 Literature Review

The first stage of this research was the targeted literature review conducted according to the themes of water, toxicology, ICP-MS and chemomstrics. The purpose of the critical analysis of the relevant literature was to examine key techniques applicable to this research and to expose gaps in the literature worthy of further investigation. This was achieved by identifying potable water quality as an area seldom investigated in contrast with raw water sources and sediments. Key techniques to be used include data collection methods and subsequent data analysis via the most sensitive analytical methods. The application of such techniques is categorised in the following sub-sections of section 3.2.

3.2.2 Qualitative Methodology

The qualitative methodology employed for this research was collection of information regarding the water distribution system owned and operated by Seqwater, the main water supplier in South East Queensland and the greater Brisbane area. Water distribution information refers to area specific water source and supply details. Additionally, sample collection participants also undertook a small survey (detailed in section 3.4.1.1) about their knowledge of their water supply system and its use within their house.

3.2.3 Quantitative Methodology

The quantitative methodology is the main methodology employed for this research and encompasses the collection and analysis of potable water samples from the greater Brisbane area. These water samples were analysed via ICP-MS. Analysis of freshly collected samples occurred as soon as possible so as to obtain the most precise data.

The 26 trace elements and heavy metals to be inspected in the course of this research are: potassium, calcium, sodium, magnesium, aluminium, antimony, arsenic, barium, beryllium, cadmium, cobalt, chromium, copper, iron, lead, manganese, mercury, molybdenum, nickel, selenium, silver, thallium, thorium, uranium, vanadium and zinc.

These elements can already be separated into groups of macroelements and microelements on the basis of previous research by Komorowicz et al. (2010). Macroelements always appear naturally in the water environment and include calcium, magnesium, potassium, sodium and iron. The remaining elements to be analysed can be classified as microelements and are expected to appear in significantly lower concentrations. The raw data collected here can be directly compared to the 2011 Australian Drinking Water Guidelines, prior to the application of statistical methodologies.

3.2.4 Statistical Methodology

The quantitative data obtained via ICP-MS analysis of water samples can be further investigated using statistical methodologies, specifically, chemometrics. Beyond basic statistics, there are a multitude of both quantitative and qualitative chemometric methods to be considered. Such methods encompass exploratory data analysis, pattern recognition, classification, multicriteria decision making, discriminant analysis, calibration, regression and prediction, among others. The software used to accomplish this methodology includes Decision Lab 2000, SIMCA P-10.0, Minitab 16 Statistical Software and Microsoft Excel. Microsoft Excel and ICP-MS software Agilent ChemStation (offline) were the programs used for the retrospective calibration of the historical data collected from 2008 to 2012, as discussed in section 4.1.1 of Chapter Four. All historical and current data then underwent the same treatment for basic statistics and the same chemometric procedures.

3.2.5 Methodology Application Plan

The administration of all of these methodologies will fulfil the research aim and objectives and therefore answer the research questions stated in section 3.1.3. The specific methodologies, the Literature Review, Qualitative, Quantitative or Statistical, pertinent to each research question are outlined in Figure 3-2.

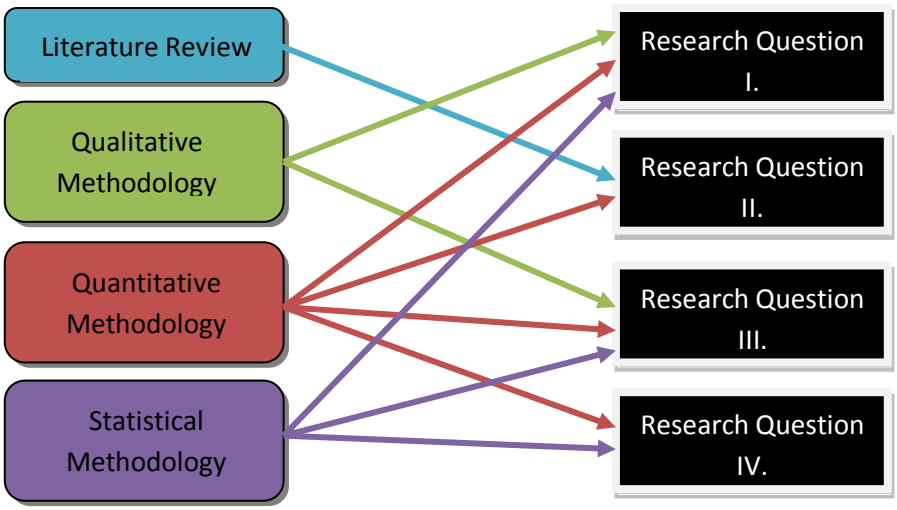


Figure 3-2. Methodologies matched to research questions.

Following the literature review, these methodologies were applied to this research in sequence, whereby background information regarding water supply and distribution was acquired prior to sample collection and survey of participants. The ensuing section 3.3 details the participants and sample collection setting for this research.

3.3 Setting and Participants

The general setting of this research is the city of Brisbane in South East Queensland. The capital city of Queensland, Australia, is the most populous city in the state and third most populous in the country. The population of greater Brisbane is 2.19 million, accounting for nearly half the population of Queensland (Australian Bureau of Statistics, 2013). Brisbane is described as extending in all directions along the floodplain of the Brisbane River valley between Moreton Bay to the east and the Great Dividing Range to the west. Brisbane is built on a low-lying floodplain, with many suburban creeks criss-crossing the city, increasing the risk of flooding. The climate in Brisbane is described as subtropical, with warm to hot weather for most of the year. Summer is the most humid time of the year for Brisbane, with average maximum temperatures around 30^{o}C and the highest rainfall, bringing thunderstorms and occasional floods. Winter is generally dry and mild with sunny days and average temperatures of around 17^{o}C (Tourism Australia, 2013).

The history of water use in Brisbane city has been explored in Chapter One. Now, in 2014, 90% of water supplied throughout South East Queensland is from Seqwater, who own and operate 26 dams, 47 weirs, 14 bores and aquifers as well as 46 water treatment facilities (Seqwater, 2013h). The greater Brisbane area is supplied with water mainly from Wivenhoe, Somerset, and North Pine Dams, as well as Baroon Pocket and Ewan Maddock Dams on the Sunshine Coast, and even Hinze Dam on the Gold Coast. Water from the Lockyer region and Wivenhoe and Somerset Dams is treated at Mt Crosby Water Treatment Plant (WTP), and water from North Pine Dam, another major source for the northern region of Brisbane, is treated at North Pine Dam WTP, prior to on sell by Seqwater. Customers in the greater Brisbane area purchase their water from the council owned Queensland Urban Utilities (formerly Brisbane Water), who also service the Ipswich, Somerset, Lockyer Valley and Scenic Rim regions, as shown in Figure 3-3.

Figure 3-3. Map detailing the water retailers used by Seqwater to deliver water to different regions of SEQ. Unitywater sells to Sunshine Coast and Moreton regions, Redland City Council sells to Redland, just as Logan City Council sells to Logan, City of Gold Coast sells to the Gold Coast, and the largest retailer, Queensland Urban Utilities supplies Brisbane, Moreton Island, Ipswich, Scenic Rim, Lockyer Valley and Somerset regions (Seqwater, 2013l). Reprinted from Seqwater – Your local water retailer, Copyright (2014), with permission from Seqwater.

The participants selected from the broader population for this research constitute a large, representative sample group and were selected as a convenience sample. This non-random sample included family, friends and colleagues who, as homeowners or tenants, allowed access to their residence for the collection of tap, filtered and/or tank water samples. Dependent upon circumstance, many participants also involved their neighbours, resulting in multiple samples per suburb. The participating suburbs of Brisbane were:

> Acacia Ridge, Albion, Albany Creek, Alderley, Annerley, Arana Hills, Archerfield, Ashgrove, Aspley, Bellbowrie, Benowa, Bracken Ridge, Brisbane CBD, Bulimba, Bunya, Carole Park, Carseldine, Chandler, Chapel Hill, East Brisbane, Enoggera Reservoir, Everton Hills, Everton Park, Ferny Grove, Ferny Hills, Fitzgibbon, Forest Lake, Gaythorne, Graceville, Greenslopes, Hamilton, Heathwood, Hemmant, Highvale, Indooroopilly, Jimboomba, Kallangur, Kangaroo Point, Kelvin Grove, Kenmore, Keperra, Lutwyche, Mackenzie, Mansfield, Mitchelton, Moorooka, Morningside, Mt Crosby, Mt Ommaney, New Farm, Paddington, Red Hill, Samford, Samford Village, Seventeen Mile Rocks, Sinnamon Park, Shailer Park, Stafford Heights, Tambourine, Taringa, The Gap, Thornlands, Toowong, Upper Kedron, Victoria Point, Wellington Point, Wilston, Windsor, Woolloongabba, Wynnum and Wynnum West.

One aim of this research was to collect a variety of potable water samples representative of the greater Brisbane area. In the instance of suburbs or large areas of Brisbane not covered by initial sample collection (through affiliation), an alternative was suggested by Bob Gray, a scientist with Scientific Analytical Services (SAS) Laboratories. SAS Laboratories are responsible for water quality testing throughout Brisbane, and specifically collect potable water samples from 19 points along the water distribution system. In rural areas where there is not a direct connection to the distribution system (in the form of a tap secured from the public in a locked box), procedure dictates that samples are collected from taps in public parks. This procedure was considered to significantly minimise areas that would otherwise go uncovered. Fortunately, the large number of participants meant that this measure did not need to be implemented.

Upon mapping sample areas prior to commencement of sample collection for this research, it became apparent that the current sample plan would sufficiently encompass the greater Brisbane area (see Figure 4-16 in Chapter Four). For this reason and also due to time constraints, the collection of 'extra' samples from public parks in Brisbane was deemed

unnecessary. It was noted that this procedure would be ideal to increase sample size should future work on this research be undertaken.

The materials, number and type, and procedure for the collection and analysis of potable water samples from the greater Brisbane area are detailed in the following sections.

3.4 Research Materials

This section can be categorised into Sample Collection and Sample Analysis materials used to conduct this research. Much of the following procedures were based on US EPA Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry (US EPA, 1994). Generally, there were few deviations from this method for the data collected and analysed in 2013, whereas there was no sample preparation performed on the samples that constitute the historical data (2008 – 2012). All materials used are thoroughly described so that the reader may replicate, or in the future, adapt and develop this methodology for their own research.

3.4.1 Sample Collection and Preservation Materials

Sample collection materials encompass the equipment and reagents required to physically collect and preserve the potable water samples, as well as the short survey developed to obtain the homeowners' or tenants' knowledge of their water supply system and its use within their residence.

The critical review of literature describing similar sample collection methods concluded that the most appropriate containers for the collection of potable water samples are PET containers. Glass containers are not considered appropriate due to element transfer between the sample and the glass. Prior to use, all PET containers in the form of 250 mL bottles (supplied by Australian Laboratory Services (ALS)) for raw and treated water samples, and 50 mL centrifuge tubes for ICP-MS for potable water samples, were soaked in a 10% nitric acid bath, requiring the use of RCI Premium 70% nitric acid and Milli-Q water, an ultrapure water with 18.2 MΩ resistivity.

During sample collection, a 50 L Esky© filled with ice was utilised to keep samples cool in transit. Once back in the laboratory, each sample was filtered into a fresh and identically labelled 50 mL centrifuge tube using a 0.45 µm Merck Millipore filter attached to the tip of a 20 mL syringe.

Both the 50 mL centrifuge tube and 20 mL syringe were similarly soaked in the 10% nitric acid bath and also rinsed with a small amount of sample. Each sample was subsequently acidified for preservation using the same RCI Premium 70% nitric acid which was previously used to make up the nitric acid bath. Finally, samples were stored in the refrigerator (at 4^{o}C) until analysis.

3.4.1.1 Participant Survey

This short survey was developed to gain information regarding the supply and use of potable water within each residence visited. All information was volunteered. The questions asked and examples of answers are provided below.

1. When was this residence built?
    - ✓ The decade a residence was built was sufficient.
2. What is the composition of household water pipes?
    - ✓ Lead (pre-1930s), galvanised pipes (1950s-1960s), copper (became less common in late 1980s, but still in use) or PVC (currently in use).
3. Do you have filtered water in your home? If so, how frequently is the water filter (in the tap/fridge/jug) changed by yourself or the company?
    - ✓ Monthly, semi-annually, annually, etc.
4. How is tank water utilised?
    - ✓ For laundry, flushing toilets, etc.
5. General comments on aesthetics of the drinking water.
    - ✓ Issues with taste, odour, colour, etc.

Answers were collated and provided insight for fingerprinting potable water sources, and on typical water quality and usage within South East Queensland.

3.4.2 Sample Analysis Materials

Analysis of potable water samples was performed using ICP-MS and based on US EPA Method 200.8. In addition to the elements analysed in Method 200.8, macroelements sodium, magnesium, potassium, calcium and iron were also selected for analysis in this research. ICP-MS requires the use of a number of standards for internal and external sample calibration, as well as two tuning solutions for the instrument. The standard solutions utilised for this research were:

- ✓ *Agilent Environmental Calibration Standard, 100 mL* (#5183-4688), which contains 1000 mg/L of Fe, K, Ca, Na and Mg; and 10 mg/L of Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn, Th and U in a matrix of 10% nitric acid (HNO_3).
- ✓ *Single Element Standard – Mercury, 100 mL* (#8500-6941), containing 10 mg/L of Hg in a matrix of 2% nitric acid (HNO_3).
- ✓ *Internal Standard Mix, 100 mL* (#5188-6525), containing 10 mg/L of ^{6}Li, Sc, Ge, Y, In, Tb and Bi in a matrix of 5-10% nitric acid (HNO_3).
- ✓ *Agilent Tuning Solution, 500 mL* (#5184-3566), which contains 1 µg/L of Li, Y, Ce, Tl and Co in a matrix of 2% nitric acid (HNO_3).
- ✓ *PA Tuning Solution*, 250 mL containing 20 mg/L each of Zn, Cd, As; 10 mg/L each of Ni, Pb, Mg; 5 mg/L each of Tl, Na Al, U, Cu, Ba, Co, Sr, V, Cr, Mn, In, Bi; and 2.5 mg/L each of Y, Yb in a matrix of 2- 5% nitric acid.

Multi-element calibration standards were freshly prepared from the Environmental Calibration Standard and Mercury Single Element Standard by diluting 1-to-20,000, 1-to-10,000, 1-to-1000 and 1-to-100 fold using Milli-Q water and RCI Premium 70% nitric acid. As a result, the standards were made up in a 1% nitric acid matrix. All such solutions were prepared in 250 mL volumetric flasks that were also soaked in a 10% nitric acid bath (as in section 3.4.1) and dried prior to use. The volumes of each standard required were delivered using Eppendorf pipettes and the mass of the delivered volume was measured to ensure the highest accuracy. RCI Premium 70% nitric acid and Milli-Q water were used in the preparation of these standard and blank solutions (i.e. when diluting "to the mark" in volumetric flasks) due to the high sensitivity of ICP-MS and also to minimise contamination. The Internal Standard Mix was uniformly added to the filtered and acidified water samples and multi-element calibration standards using Eppendorf pipettes, where the volume delivered was also weighed.

The Pulse/Analog Tuning Solution was prepared to mimic Agilent's *PA Tuning Solution*, whereby the appropriate volumes of single element solutions were used to achieve the correct concentrations, and the solution was made up with RCI Premium 70% nitric acid and Milli-Q water so that the solution was in a 5% nitric acid matrix.

Prepared standards and samples were then analysed via ICP-MS. The materials required for use with this instrumentation include the aforementioned Tuning Solution to appropriately tune system wide parameters, the PA Tuning Solution to specifically tune the pulse/analog factors, as well as a freshly prepared 5% v/v nitric acid wash solution for during the sample run. The 50 mL sample tubes were placed in sequence in four 3 x 7 (21 place) sample racks and locked into the sample area of the instrument.

Nitric acid is consistently used in all Standard Calibration, Tuning and Internal Standard Mix solutions and elsewhere throughout this method, because nitric acid is preferred by ICP-MS in order to minimise polyatomic interferences (US EPA, 1994).

3.5 Water Sample Collection and Preservation Procedure

In line with the previous section (3.4 Research Materials), this section will describe the specifics of the samples collected and preserved, and outline how these research materials were used for historical samples and samples for current research. The procedures that were followed to ensure the highest precision and accuracy and why these procedures were chosen will also be discussed.

The gap in the knowledge area being fulfilled by this research is the determination of trace element and heavy metal content of potable water in the greater Brisbane area. To do this, a variety of potable water samples were analysed. The potable water samples collected in 2013 from numerous households around Brisbane included tap, filtered and tank water samples. Not all households had filtered water or tank water, therefore, the number of filtered and tank water samples were significantly less than the number of tap water samples collected.

For this research to be scientifically significant, the number of samples collected must at least double, preferably triple, the number of variables being tested. In this research 26

trace elements and heavy metals are the dependant variables being tested, where the water samples collected are considered independent objects. Therefore, approximately 80 potable water samples were desired for a thorough analysis. In total, 102 tap water samples, 45 filtered water samples and 32 tank water samples were collected from homes in the greater Brisbane area for this research.

Additionally, nine raw water samples were collected from Mt Crosby Water Treatment Plant, College's Crossing (on the Brisbane River), Oxley Creek, Wivenhoe Dam, Lake Somerset, Baroon Pocket Lake and Dam, Ewan Maddock Dam, and Forgan Cove and Bullocky Rest from Lake Samsonvale (North Pine Dam). Two treated water samples were collected from Mt Crosby West Bank Water Treatment Plant, one from each reservoir on Cameron's Hill; and 20 mains water samples were collected from the water distribution system through the use of a standpipe. Finally, 11 brands of bottled water were also purchased for analysis. Overall, a total of 221 water samples were collected in 2013 for this research.

3.5.1 Procedure for Collection of Samples 2008 – 2012

Additionally, 218 samples were collected from 2008 to 2012, forming the basis of the longitudinal study for this research. This historic data was collected as part of a third year undergraduate student practical performed at QUT over successive years with different student cohorts from 2008 to 2012. Students were supplied with 50 mL capped plastic centrifuge tubes for ICP-MS and tasked with the collection of tap, tank and filtered water from their homes, resulting in waters from a variation of post codes. Numerous brands of bottled water were also collected, totalling six different brands over the five year span. The nature of collection dictated no pre-treatment or preservation of the water samples collected before analysis via ICP-MS.

3.5.2 Procedure for Collection and Preservation of Samples for Current Research (2013)

The procedure followed for sample collection and preservation was developed based on US EPA Method 200.8, which states that dissolved elements can be determined after suitable filtration and acid preservation with the addition of nitric acid (US EPA, 1994). Additionally, the critical review of the literature revealed that the majority of authors were unanimous on the materials and processes used, thereby cementing the procedures used.

A total of 200 x 50 mL PET centrifuge tubes and up to 50 x 250 mL PET bottles were soaked in a 10% nitric acid bath for several days (at least 24hrs). An extra 250 (duplicate) 50 mL PET centrifuge tubes and 20 mL syringes were similarly soaked in a 10% nitric acid bath, as these would be required for filtering and sample preservation after samples were collected and bought back to the laboratory. This soaking step was crucial for minimising potential contamination and ion exchange between the sample and the collection containers. After the collection containers were soaked for a sufficient period of time, they were removed from the nitric acid bath, emptied, sealed, and the outside of the tubes were dried for transport to the sample areas.

Quality control measures taken for sample collection included the preparation of two field blanks and a trip blank. The field blanks were used to demonstrate that the sample collection procedure was not introducing contamination to the samples. Both field blanks were mock samples collected from the laboratory tap in 50 mL sample containers, placed in the Esky© and transported along with all other samples throughout the day so that they were exposed to the same environment as the real samples. Once back at the laboratory, each field blank underwent a different part of the preservation procedure so the source of any contamination could be differentiated. That is, one field blank was filtered with the 0.45 µm Merck Millipore filter but not acidified (**FBF**); the second field blank was not filtered, but was acidified with RCI Premium 70% nitric acid to pH≤2 (**FBA**). Similarly, the trip blank was a mock sample collected in a 50 mL sample container from the E517 laboratory tap. This trip blank served to identify contamination that could have occurred during sample transport and analysis, rather than as a result of sample collection or preservation in the field or laboratory. Therefore, the trip blank (**TB**) was similarly placed in the Esky© and transported with the other 50 mL sample containers throughout the day and then back to the laboratory for analysis with the collected samples. All field and trip blanks were measured to 40 mL and had 40 µL of Internal Standard added for instrumental analysis.

Tap, filtered and tank water samples were all collected in the same manner. Water was run from the collection point, i.e. tap, for several seconds so that water samples would be "flushed". This was done so that any build up of heavy metals or trace elements in the pipes following long periods of disuse would not taint the representative sample collected. Each sample collection tube was rinsed three times with the water it was to contain before the sample was collected and the container sealed. Every sample tube was filled to capacity, resulting in 50 mL of sample collected each time.

Samples were appropriately labelled with a water type and number corresponding to the residence visited, and all information was recorded in the Sample Collection spreadsheet. For example, water type could be: **T** for tap water; **TK** for tank water, and **F** for filtered water. Additionally, if the first residence visited provided tap and tank water samples, they were labelled T1 and TK1 respectively; if the second residence visited provided tap and filtered water samples, they were labelled T2 and F1 respectively. Labelling continued in this manner and, as a result, sample types were labelled in the sequence in which they were collected. Samples were then stored in an Esky© full of ice to preserve them by keeping them cool as they were transported back to the laboratory.

The collection of raw water samples in 250 mL PET bottles from dams and creeks adhered to a similar process of container rinsing and labelling – whereby raw water samples were denoted by the initials of the site from which they were collected. For example, samples from Wivenhoe Dam and Lake Somerset were labelled **WD** and **LS** respectively. Extra information regarding the site location and surroundings were recorded, followed by temporary refrigeration of samples in the Esky©. The collection process for the purchased bottled water samples involved taking all bottled waters to the laboratory, where sample type was distinguished by the letter **B** on freshly washed sample tubes, rinsing these sample tubes three times with the bottled water brand they were to contain, and filtering approximately 40 mL of bottled water into the sample tube.

Collaboration with H_2Flow, Brisbane and South East Queensland's leading water services business, resulted in the collection of additional samples. The 250 mL containers that had been washed in the 10% nitric acid bath were left with the company the week leading up to sample collection. A further 19 water samples were collected. Of these, 16 were tap water samples, two were mains water samples and one water sample was taken from within a water truck. These water samples were labelled with **H** to distinguish them from other tap and mains water samples collected, as these samples experienced a delay in the filtering and acidification process because they were collected over a weekly period. However, upon collection, samples were refrigerated until they could be retrieved.

The day after potable sample collection, 17 mains water samples were collected from the distribution system through a standpipe. These samples were collected in 250 mL PET bottles (supplied by ALS) and labelled with **MW** (for mains water), followed by the initials of the area from which the sample was collected. For example, the mains water sample

collected from Sumner Park was labelled **MWSP**. A description of the condition of the fire hydrant used and estimates of the age of each area visited were also recorded.

Upon returning to the laboratory each day, the appropriate number of freshly soaked 50 mL centrifuge tubes were labelled identically to the collected samples, with the addition of an asterisk (*****) to denote that the sample had been filtered and acidified. Each sample was transferred to a 20 mL syringe that had also been soaked in a 10% nitric acid bath and rinsed with a small amount (less than 5 mL) of sample. Then, by attaching a 0.45 µm Merck Millipore filter to the syringe, 40 mL of each sample was filtered into the fresh centrifuge tube (which was also rinsed with a small amount of sample). Although the water samples collected throughout this research were of drinking water quality (with the exception of the nine raw water samples), filtration was deemed a necessary step due to the sensitivity of the ICP-MS instrumentation. Furthermore, all samples were acidified to pH≤2 by adding 3 drops of RCI Premium 70% nitric acid with a Pasteur pipette in an effort to minimise polyatomic interferences when analysed using ICP-MS. The number of drops of RCI Premium 70% nitric acid required to lower the pH of the sample to ≤2 was determined daily with a "dummy" sample, whereby a 50 mL sample tube was filled to 40 mL with tap water from the laboratory (E517) and drops of RCI Premium 70% nitric acid were singularly added until pH≤2 was achieved. This preservation procedure is identical to that described in US EPA Method 200.8.

There was also 40 µL of the Internal Standard Mix (#5188-6525), containing 10 mg/L of ^{6}Li, Sc, Ge, Y, In, Tb and Bi in a matrix of 5-10% nitric acid added to each sample collected. It was suggested in US EPA Method 200.8 that internal standardisation can be effectively used to compensate for many physical interference effects, where the internal standard elements ideally have similar analytical behaviour to the elements being determined (US EPA, 1994). The chosen volume of 40 µL of Internal Standard added to 40 mL of sample resulted in an Internal Standard concentration of 10 parts per billion in every sample analysed. The 40 µL of Internal Standard was delivered to each sample tube using the same pipette tip (per day for six days). The volume delivered was also measured by mass to ensure maximum accuracy.

Samples were then refrigerated at 4^{o}C, thus finalising sample preservation. Samples that are properly preserved upon receipt in the laboratory, as described in the above procedure, can be stored in this manner for up to six months before analysis (US EPA, 1994).

3.5.3 Procedure for Preparation of Standards for Sample Analysis

Just as the materials for the collection and preservation of samples were soaked in a 10% nitric acid bath, so too were the five 250 mL volumetric flasks and 50 mL centrifuge tubes used for standard preparation. The volumes of the Agilent Environmental Calibration Standard and the Mercury Single Element Standard (the Certified Reference Materials (CRMs)) required to make up the set of (external) calibration standards and blank solution were calculated and are displayed in Table 6-1 in Appendix B.

The mass of each volume of the calibration standard added with the Eppendorf pipettes was also measured to ensure maximum accuracy. Following the addition of the correct volumes of each Agilent Standard to the 250 mL volumetric flasks using 100, 1000 or 5000 µL Eppendorf pipettes, the flasks were diluted to the mark with 3.5 mL of RCI Premium 70% nitric acid and the remaining volume with Milli-Q water. As a result, standards were made up in a 1% nitric acid matrix. The flasks were inverted to ensure thorough mixing and no concentration gradient within each calibration solution. Finally, 40 mL of each calibration solution was transferred into a rinsed and labelled centrifuge tube, and 40 µL of Internal Standard was added ready for analysis using ICP-MS.

The analysis of the variety of potable water samples collected took place on two experimental platforms: direct analysis via ICP-MS and analysis of data through the use of chemometrics. The procedure for the analysis of standard solutions and all samples collected is detailed in the following Instrumentation and Procedure section.

3.6 ICP-MS Instrumentation and Procedure

Linking directly to the previous section 3.5 Samples and Procedure, this section will detail all components of the ICP-MS instrumentation used as well as the procedure used to analyse the samples collected and the standard solutions prepared, for both historical samples and current samples collected for this research.

3.6.1 Inductively Coupled Plasma – Mass Spectrometry Instrumentation

ICP-MS instrumentation is extensive and vital to the precise analysis of trace and ultratrace samples. The instrument used for this research was the Agilent 7500ce unit. The components of the Agilent 7500ce ICP-MS, released in 2004, are as follows:

- Open sample introduction area
- Temperature controlled Spray Chamber
- Robust Plasma
- Interface and Ion Lens
- Active Mass Flow Control (AMFC) – controls all standard gas flows
- Octopole Reaction System (ORS)
- Vacuum System and Analyser
- Advanced Detection System (Agilent Technologies Inc., 2004a).

The basic theory behind ICP-MS begins with sample introduction and nebulisation with high temperature (10,000K) and high velocity argon plasma. Analyte elements are ionised by collisions with argon ions, excited argon atoms, or excited electrons in the argon plasma. The plasma is then directed into the mass spectrometer, which separates and detects ions based on their mass-to-charge ratio.

ICP-MS is capable of analysing solid and liquid samples. Solid samples require laser ablation, whereas aqueous samples are introduced by way of a nebuliser, which aspirates the sample, forming a fine mist. The temperature controlled spray chamber then removes larger droplets of mist via a drain.

Once the aqueous sample has been passed through the nebuliser and is partially desolvated, the mist travels into the torch body, the end of which is placed inside an induction coil used to transmit a radio-frequency electric current to the argon plasma. The high temperature argon plasma, contained in a quartz tube and ignited by a 27.12 MHz radio frequency, is used to rapidly dry, decompose, vaporise, atomise and ionise each atom (Agilent Technologies Inc., 2005b). The high temperature, stability and relatively inert argon environment in the plasma eliminates much of the interference encountered with flames when atomising samples (Harris, 2007). The accelerated electrons produced from this ignition step collide with argon atoms, sometimes producing molecular ions such as ArO^+, Ar_2^+ and $ArCl^+$ and eventually balancing the rate of recombination of electrons with argon ions, producing a stream that consists mostly of argon atoms with a small fraction of free electrons and argon ions.

The inherent problem lies in the fact that ICP-MS is relatively inefficient; only one out of every million ions generated in the plasma actually reaches the detector (Thomas, 2001-2002). As a result, the interface region is considered one of the most critical areas of the whole ICP-MS system. The role of the interface region is to transport ions efficiently from the plasma, which is at atmospheric pressure, to the mass spectrometer which is in a vacuum. The pressure is reduced at each successive section of the instrument; several pumps are utilised to gradually reduce the pressure before the ion stream reaches the quadrupole. This is done through the use of water-cooled sampler and skimmer cones, both with very small orifice diameters of 0.8-1.2 mm and 0.4-0.8 mm respectively (Thomas, 2001-2002).

The sampler and skimmer cones are made of nickel and platinum respectively, and are maintained at a vacuum in the 7500ce instrument. When ions emerge from the skimmer cone they are directed through the ion optics. The extraction lens behind the skimmer cone has a high negative potential to attract positive ions from the plasma. The ion focusing system is positioned between the skimmer cone and the mass separation device and consists of one or more electrostatically controlled lens components. The role of this ion focusing system is to transport the maximum number of ions from the plasma environment at atmospheric pressure to the mass separation device, at the same time rejecting as many matrix components and non-analyte based species, such as particulates, neutral species and photons, as possible (Thomas, 2001-2002).

The Agilent 7500ce instrument contains an Octopole Reaction System (ORS) that is highly efficient in the removal of interferences. This collision/reaction cell significantly improves sensitivity and detection limits using hydrogen (H_2) as a reactive gas, and helium (He) as a collision gas. The Octopole Reaction System eliminates multiple polyatomic interferences for critical elements such as arsenic, selenium, chromium, potassium, calcium, vanadium and iron, without the need for highly reactive gases, as well as removing interferences without matrix matching, element-specific optimisation or interference equations (Agilent Technologies Inc., 2004b). Such elements suffer from major spectral interferences generated by ions derived from the plasma gas, matrix components or the solvent/acid used in the sample (Thomas, 2001-2002). Here, interference is defined as any effect that changes the signal while analyte concentration remains unchanged. The interference of ions with a common mass is called isobaric interference. Polyatomic interferences arise from the argon plasma background, which usually contains hydrogen and oxygen from dissociation of water vapour, nitrogen and carbon dioxide from entrainment of atmospheric air and concomitant ions from the sample or standard solutions such as chlorides and nitrates. Potential interferences and how these may be overcome with the ORS are listed in Table 3-1.

Table 3-1. Common interferences and solutions for major ions in ICP-MS (PQB513 Instrumental Analysis, 2010; Thomas, 2001).

Analyte	Isotope	Potential Interferences	Alternatives with ORS
K	39	^{38}ArH	React with H_2 or bombard with He to dissociate ion.
Ca	40	$^{40}Ar^+$	Use ^{43}Ca or ^{44}Ca isotope.
Ti	47	CCl^+	React with H_2 or bombard with He to dissociate ion.
V	51	$^{16}O^{35}Cl^+$	
Cr	52	$ClOH^+$, $^{40}Ar^{12}C^+$, $^{38}ArNH^+$	
Cr	53	$^{38}ArNH^+$	
Mn	55	$^{38}ArNH_3^+$	
Fe	56	$^{40}Ar^{16}O^+$	React with H_2 or bombard with He to dissociate ion; OR use alternative isotope.
Fe	57	$^{40}ArOH^+$	
As	75	$^{40}Ar^{35}Cl$	
Se	76	$^{38}Ar^{2+}$	H_2 gas attaches to Ar complex and shifts the signal up one mass unit OR can break it down into a neutral diamer.
Se	77	$^{40}Ar^{2+}$	
Se	78	$^{38}Ar^{40}Ar^+$	
Se	80	$^{40}Ar^{40}Ar^{(2+)}$	

The mass analyser is next in sequence in ICP-MS instrumentation. The quadrupole mass analyser in the Agilent 7500ce unit is positioned between the ion optics and the detector. Ions pass from the ion focussing system into the analyser vacuum stage, where they are separated by the quadrupole according to their mass-to-charge ratio (Agilent Technologies Inc., 2005b). A quadrupole consists of four cylindrical metallic rods in parallel, of the same length and diameter, arranged in a square (Thomas, 2001-2002). High frequency AC and DC voltages are applied to the two pairs of rods; this frequency is 3 MHz in the Agilent 7500ce instrument (Agilent Technologies Inc., 2004a). The AC (same voltage but out of phase between the two pairs of rods) and DC (positive on one pair and negative on the other) voltages give a dynamic hyperbolic electric field, in which any ion above or below the set mass of the quadrupole enters an unstable trajectory and collides with the rods. Therefore, by varying these voltages, the rods act as a mass filter allowing only ions of a specific mass-to-charge ratio to pass through the centre of the quadrupole at any given combination of applied voltages (Agilent Technologies Inc., 2008). Since these voltages can be changed very rapidly (100 milliseconds), the elemental mass range from 2 to 260amu can be scanned very quickly, giving a mass spectrum for all elements and their isotopes (Li to U), that is acquired virtually simultaneously (Agilent Technologies Inc., 2005b). As in this research, many combinations of voltages were chosen, thus allowing a varying array of ions to be detected.

The ions of the trace elements and heavy metals of interest are subsequently detected by an electron multiplier detector. An electron multiplier generates a measureable signal pulse from the impact of a single ion (Agilent Technologies Inc., 2005b). A positive ion arrives at the mouth of the detector and is deflected to the first negatively charge dynode. The impact of the ion releases several free electrons from the dynode surface, which are repelled from the negative voltage and strike the next dynode. Each electron which strikes the second dynode releases several electrons from that surface and so on, significantly multiplying the signal (Agilent Technologies Inc., 2005b). The detector is positioned off-axis to minimise the background from stray radiation and neutral species coming from the ion source (Thomas, 2001-2002). A dual mode detector is employed and operates in two modes: pulse mode for low sample concentrations, and analog mode for high sample concentrations (Agilent Technologies Inc., 2008). Pulse mode detects signals at lower count rates, typically up to a few million counts per second (cps) based on each individual ion impact, whereas analog mode measures the current generated by the electron stream (Agilent Technologies Inc., 2005b).

In terms of dynamic range, up to nine orders of magnitude of concentrations can be detected. This is again broken down into pulse counting and analog counting modes. Pulse counting mode is typically linear from zero to about 10^6 counts per second (cps), and analog counting is suitable from 10^4 to 10^9 counts per second (Thomas, 2001-2002). Cross calibration of pulse and analog calibration curves is performed to cover all concentrations levels, which is especially important for elements with concentration levels that could generate both pulse and analog signals. Following cross calibration, both pulse and analog calibration curves are normalised, which means the detector is suitable for concentrations levels between 0.1 ng/L (ppt) to 100 mg/L (ppm) (Thomas, 2001-2002).

In summary, for this research, the Agilent 7500ce ICP-MS instrument utilised an off-axis ion extraction system that reduces mass bias across the mass range and ensures low background counts; an octopole reaction and collision cell for reducing interferences from polyatomic ions; a quadrupole with a hyperbolic cross-section for high resolution and a detector which uses pulse mode for low counts and analog mode for high counts, for a combined linear concentration range of 10^9.

3.6.2 Procedure for Inductively Coupled Plasma – Mass Spectrometry

The Agilent 7500ce ICP-MS instrument detailed in the previous section was used for the analysis of water samples collected from 2008 to 2012 by students, and in 2013 for this research. Due to the nature of this technique, no sample preparation was required beyond the sample collection and preservation techniques previously described. In general, the operating conditions recommended by Agilent Technologies Inc. were followed.

The accompanying software to this instrument is Agilent ChemStation. Initially, the ICP-MS instrument was tuned using Agilent Tuning Solution, which contains 1 µg/L of Li, Y, Ce, Tl and Co in a matrix of 2% nitric acid. Following the overall instrument tune, the pulse and analog counting signals were similarly tuned using the PA Tuning solution containing 20 mg/L each of Zn, Cd, As; 10 mg/L each of Ni, Pb, Mg; 5 mg/L each of Tl, Na Al, U, Cu, Ba, Co, Sr, V, Cr, Mn, In, Bi; and 2.5 mg/L each of Y, Yb in a matrix of 5% nitric acid. Several dilutions were prepared to cover a range of sensitivity, and therefore ensure that tuning for all elements in the PA Tuning solution was completed. PA Tuning solution dilutions included the original solution, then 1:10, 1:30, 1:100 and 1:200 dilutions.

For all subsequent instrument tunings, the detector parameters were excluded, as adjustment of these parameters would nullify the carefully tuned pulse/analog factor. The P/A Factor Tuning Report is presented in Figure 6-4 in Appendix B.

Agilent ChemStation was then used in Quantitative Analysis mode to set up an analysis method and to accurately measure the concentrations of specific elements in the unknown samples. Multi-level calibrations were constructed from four concentrations (plus a blank) of multi-element calibration standards containing all of the analytes of interest to this research.

Data acquisition was arranged in Agilent ChemStation by the selection of elements from the periodic table, whereby the software automatically chose the most abundant isotope free from interference. The method and elements of interest were based on US EPA Method 200.8, and additional elements, isotopes and tuning steps were added for the purpose of this research.

The elements and isotopes chosen in the analysis of water samples collected in 2013 for this research, and water samples collected from 2008 to 2012 as part of the longitudinal study carried out by undergraduate students, are all detailed in Table 3-2.

Table 3-2. The isotopes of trace elements and heavy metals analysed in water samples collected in 2008 - 2012, and in 2013. The additional elements analysed in 2010 only were internal standard elements that were incorrectly included in the quantitative analysis performed.

Elements	Isotopes	
	2008 – 2012	2013
Li	6, 7	
Be	9	9
Na	23	23
Mg	24	24
Al	27	27
K	39	39
Ca	43, 44	40, 43, 44
V	51	51
Cr	52, 53	52
Mn	55	55
Fe	56, 57	56, 57
Co	59	59
Ni	60	60
Cu	63	63
Zn	66	66
As	75	75
Se	78, 82	78
Mo	95	95
Ag	107	107
Cd	111	111
Sb	121	121
Ba	137	137
Hg	202	202
Tl	205	205
Pb	206, 207, 208	208
Bi	209	
Th	232	232
U	238	238
	2010 (only)	
Sc	45	
Ge	72	
Y	89	
In	115, 118	
Tb	159	
Er	166	

The Octopole Reaction System was filled with hydrogen gas, helium gas or no gas, to react or collide with background ions in order to dissociate them and minimise interference. As a result, individual concentrations for each of these tuning steps, labelled [#1] for hydrogen gas, [#2] for helium gas, and [#3] for no gas, were collected for the isotopes of the trace elements and heavy metals of interest throughout this research.

Isobaric interferences were checked for by measuring the isotope ratios and were predicted and compensated for through the application of interference equations. The interference equations applied in this method were recommended by Agilent ChemStation software and are detailed below. Bracketed element isotopes are added (or subtracted) to give the main isotope concentration.

$$Lithium\ 6 = Li^{(6)} - (Li^{(7)} \times 0.082)$$
$$Indium\ 115 = In^{(115)} - (In^{(118)} \times 0.014)$$
$$Lead\ 208 = Pb^{(206)} + Pb^{(207)} + Pb^{(208)}$$

Finally, the sampling sequence was set up using this same software. For the number of samples collected (a total of 226 samples including duplicates, test and field blanks, plus five standards to be included in each run), three separate runs were required as there were only 84 sample places available per run. Each sequence was identical and began with a wash with the 5% nitric acid solution, followed by the analysis of the blank and four standard solutions prepared, and then another wash with the 5% nitric acid solution. Analysis of samples was next in sequence, and for every 10 samples analysed, Standard 2, Standard 3, or Standard 4 (see Table 6-1 in Appendix B) were analysed again (in that order) as "checks" to combat instrument drift and give insight into the recovery of each element. Following checks using Standard 4, a wash with the 5% nitric acid solution was performed again. This was because Standard 4 possessed the highest concentration of elements of all the standards, and so a wash was deemed necessary to ensure no contamination of future samples. All samples and standards contained Internal Standard to allow smooth checks of standards amongst samples and to correct for instrument drift and physical interferences.

Quality assurance measures involved in this procedure included the careful and appropriate labelling and organisation of samples, and the use of the Agilent Environmental Calibration Standard, Mercury Single Element Standard, Internal Standard Mix, and two tuning solutions (Instrument and PA Factor) fit for purpose. Quality control measures including verification of the hardware and software were undertaken prior to operation of the

instrument, whereby the cooling water, gas supplies, vacuum, peristaltic pump and tubing, fume exhaust, software system set up and error log were checked.

Agilent ChemStation was used to define tuning and acquisition parameters of the Agilent 7500ce ICP-MS instrument. Water-cooled nickel and platinum sampling and skimmer cones were used respectively. The temperature controlled sample introduction system utilised a peristaltic pump to introduce samples to the argon plasma via a concentric nebuliser. Instrument operation was completely automated. The typical operation criteria for this instrument are listed in the Operator's Manual (Agilent Technologies Inc., 2005a) and displayed in Table 3-3 for each Tuning Mode, and these criteria underwent minor adjustments in order to optimise the analysis. The method was setup and data collected in Spectrum Analysis (Multi Tune) acquisition mode.

Table 3-3. Typical values of tuning parameters in Standard (no gas), H_2 and He modes (Agilent Technologies Inc., 2005a).

Tuning Parameters	Typical Values		
	Standard Mode	H_2 Mode	He Mode
RF Power (W)	1500	1500	1500
Sampling Depth (mm)	8	8	8
Carrier Gas (L/min)	0.9	0.9	0.9
Makeup Gas (L/min)	0.15	0.15	0.15
PeriPump 1 (rps)	0.1	0.1	0.1
S/C temp (^{o}C)	2	2	2
Extract 1 (V)	4.0	4.0	4.0
Extract 2 (V)	-140	-140	-140
Omega Bias-ce (V)	-22	-22	-22
Omega Lens-ce (V)	1.2	1.2	1.2
Cell Entrance (V)	-26	-26	-26
QP Focus (V)	2	-15	-15
Cell Exit (V)	-30	-30	-30
OctP RF (V)	150	150	150
OctP Bias (V)	-6	-18	-18
QP Bias (V)	-3	-3	-16
Gas (mL/min)	N/A	5	3.5

The instrument settings and tuning parameters (most commonly) used over the five years from 2008 to 2012 are detailed in Table 3-4.

Table 3-4. Tuning and method parameters for ICP-MS used over the five year longitudinal study period (2008-2012). Some parameters may have been altered over this time period.

Tuning Parameters	Instrument Settings
RF Power (W)	1200
Sampling Depth (mm)	8
Carrier Gas (L/min)	1
Makeup Gas (L/min)	*unknown*
PeriPump (rps)	0.1
S/C temp (^{o}C)	2
Extract 1 (V)	0
Extract 2 (V)	-140
Omega Bias-ce (V)	-26
Omega Lens-ce (V)	0
Cell Entrance (V)	-38
QP Focus (V)	-8
Cell Exit (V)	-76
OctP RF (V)	180
OctP Bias (V)	-9
QP Bias (V)	-3
Gas (mL/min)	**H_2 & He:** *unknown*
Method Parameters	
Replicate samples	3
Stabilisation Time	5 secs
Curve Fit	Y = aX +b

Three tune steps involving the use of no gas, H_2 (reaction) gas and He (collision) gas in the Octopole Reaction System (ORS) were used to analyse the elements of interest according to the specifications detailed in Table 3-4. Each of these tune steps had a five second stabilisation time. Total acquisition time for each sample varied from 54.78 seconds to 208 seconds year to year due to the inclusion and/or exclusion of elements and tuning steps.

The tuning and method parameters used specifically for this research, conducted in 2013, are detailed in Table 3-5.

Table 3-5. Tuning and method parameters for ICP-MS used for this research in 2013.

Tuning Parameters	Instrument Settings
RF Power (W)	1550
Sampling Depth (mm)	8
Carrier Gas (L/min)	0.85
Makeup Gas (L/min)	0.16
PeriPump (rps)	0.1
S/C temp (^{o}C)	2
Extract 1 (V)	0
Extract 2 (V)	-140
Omega Bias-ce (V)	-26
Omega Lens-ce (V)	0
Cell Entrance (V)	-38
QP Focus (V)	0
Cell Exit (V)	-60
OctP RF (V)	180
OctP Bias (V)	-9
QP Bias (V)	-3
Gas (mL/min)	**H_2:** 3.5 **He:** 4.5
Method Parameters	
Replicate samples	3
Stabilisation Time	30 secs
Curve Fit	Y = aX +b

Again, tune steps 1, 2 and 3 involved the use of hydrogen (reaction) gas, helium (collision) gas and no gas respectively in the Octopole Reaction System (ORS), and were used to analyse the elements of interest according to the specifications detailed in Table 3-5. Each of these tune steps had a 30 second stabilisation time. Total acquisition time for each sample was 309 seconds, resulting in each run taking over 12 hours in total. The acquisition time was considerable due to the large number of elements analysed, in addition to the analysis of all Internal Standard elements.

Upon completion of data collection via ICP-MS analysis, all trace element and heavy metal concentration data for each individual sample was combined in an Excel spreadsheet for further investigation. Data pre-treatment methods were applied prior to analysis of the raw data and chemometric analyses. Following data pre-treatment, concentrations were initially compared directly to the 2011 Australian Drinking Water Guidelines.

3.7 Chemometric Analyses

Multivariate statistical techniques are ideal for the analysis of large data sets. Consequently, multiple techniques were used to investigate the data acquired from the ICP-MS analysis of trace element and heavy metals in water samples. These methods include Principal Component Analysis (PCA), Hierarchical Cluster Analysis (HCA), Preference Ranking Organisation METHod for Enrichment Evaluation and Graphical Analysis for Interactive Assistance (PROMETHEE and GAIA) and Partial Least Squares (PLS) analysis. All chemometric analyses were similarly performed on data accumulated from 2008 to 2012 as well as current data collected specifically for this research in 2013. The data matrix for each year considered all water samples objects; and all tuning steps for all trace element and heavy metal isotopes were included as individual variables for all chemometric techniques. This unanimity from pre-treatment to the application of a variety of techniques allowed easy comparisons across all years of data.

3.7.1 Retrospective Calibration of 2008-2012 Data

Initial analysis of the historical data collected as part of this longitudinal study from 2008 to 2012 revealed an error in calibration between the pulse and analog count signals. Review of the standard calibration plots displayed an obvious disagreement between the different signal counts, leading to undesirably low coefficients of correlation (R^2 values, where 1 is the greatest correlation).

When a sample is analysed via ICP-MS, the analyte signal can be collected as a pulse count or an analog count. These count signals can be tuned in the set-up software prior to performing the analysis. However, upon re-examination, it is believed that the tuning and calibration between pulse and analog counting was not successful. Therefore, the data collected had to be reprocessed, and a retrospective calibration was performed between the pulse and analog factors. This was done by determining a pulse/analog ratio for each element. This ratio was based on the slopes of the original standard calibration curves. That is, the pulse slope of the calibration curve was found when all analog points were removed; similarly, the analog slope was found when all pulse points were removed.

As there were more pulse points than analog points, the pulse/analog ratio was applied to the analog points for each element. The calibration curves were then recreated, and the unknown sample concentrations calculated from these new calibration curves. This approach was deemed successful as the coefficients of correlation were generally seen to be far more accurate. Therefore, the raw data for years 2008 through to 2012 now consisted of the recalculated sample concentrations which were to undergo further analysis.

3.7.2 Analysis of Raw Data

Raw data refer to the concentrations of the trace elements and heavy metals of interest in each sample determined from the counts per second collected in the mass spectrum. The concentration data were transferred from FileView, an Excel-like program compatible with Agilent ChemStation. The data matrix was arranged so that objects were in rows and variables in columns; that is, one row represented one sample (object), and each column represented each tuning step of each element (variable) analysed. Once in Excel, basic statistics relating to the raw trace element and heavy metal concentration data were determined. These basic statistics included: the total number of samples, missing sample data (if certain isotopes or tuning steps were not collected in different batches analysed within a year), elemental concentration mean and geometric mean, standard deviation, standard error, and minimum, maximum, range, median and quartile values.

Prior to comparing the data to the 2011 Australian Drinking Water Guidelines or the application of any chemometric techniques, the data had to undergo pre-treatment in order to eliminate discrepancies such as missing and negative values.

3.7.3 Data Pre-Treatment

Data pre-treatment is a relatively simple yet integral step that must be performed prior to any chemometric analysis. For this research, all data collected from 2008 to 2013 underwent the same pre-treatment processes for continuity. The majority of pre-treatment was performed in Excel. Following the determination of basic statistics for all data, negative and missing values were replaced to ensure a complete data set acceptable for use in the various multivariate statistical programs employed.

In this research, concentrations that were below the detection limit were displayed as negative numbers in the data matrix from the ICP-MS Agilent ChemStation software. It is not possible to have negative elemental concentrations in environmental data, simply due to the logical fact that a trace element or heavy metal is either present in the environment in a positive quantity, or it is not present at all. As a result, half of the Method Detection Limit (MDL) concentration was used to replace values that were below the MDL. The MDL was determined to be one third of the lowest positive concentration returned for each variable. This approach to data pre-treatment in this research is justified by Brereton (2009), who states that if few negative values are reported and no particular significance is placed on undetected variables, using half the minimum measurement can be a good alternative to the loss of information.

Missing data were a consequence of including or excluding different isotopes and/or tuning steps between batches within a year. For data collected in 2013, there were also very few instances when no data was available because the detector was overloaded. This occurred for macroelements sodium, magnesium and potassium in several water samples. Therefore, after any negative values were replaced with half of the MDL, any missing data was replaced by the geometric mean for the column (or variable); that is, the geometric mean for the particular tuning step of an element.

In some cases, all concentrations of one element were below the MDL, hence all data was negative. As a result, the method used to calculate the MDL could not be applied. Where many measurements are missing altogether, it is necessary to consider whether samples or variables with missing values should be removed from the data matrix (Brereton, 2009). Consequently, several trace elements and heavy metals were removed from further analysis. For 2009 data, all tuning steps for beryllium were removed prior to the application of chemometric analyses. For 2010 data, variables including tuning steps [#2] and [#3] for iron (isotope 56), cobalt (isotope 59) and selenium (isotope 78), tuning step [#2] for silver (isotope 107), tuning step [#1] for indium (isotope 115) and tuning step [#3] for mercury (isotope 202) and bismuth (isotope 209), were all removed from the data matrix for this year. Finally, for 2011 data, only tuning step [#1] for thallium (isotope 205) was removed from further analysis. No variables required removal for data collected in years 2008, 2012 and 2013. Following this pre-treatment stage, the trace element and heavy metal concentration data for each sample could be directly compared to the 2011 Australian Drinking Water Guidelines.

The replacement of negative values and missing data was the extent of the pre-treatment performed before the data were imported into several multivariate statistical programs. There are several useful data pre-treatment methods applicable for chemometric analysis, but the method used in this research was auto-scaling (also known as Z-scores transformation). Auto-scaling is a combination of individual pre-treatment methods, mean centring and standardisation. Mean centring involves calculating the mean of each column, which is then subtracted from each cell in that column, thus removing any differences in size or importance of measurements in the data set. Standardisation (or variance scaling) is achieved by dividing each variable concentration in the data set by the standard deviation of that variable. Standardisation is used to remove weighting that is artificially imposed by units of the variables. Therefore, the combination of these two methods produces data with zero mean and unit variance (i.e. standard deviation of 1), making auto-scaling a method of choice.

Auto-scaling was performed automatically on data imported into SIMCA P-10. In Minitab 16 Statistical Software, all variables were auto-scaled by selecting the "Standardise variables" option for HCA. Data imported into DecisionLab 2000 for ranking using PROMETHEE and GAIA did not undergo auto-scaling, because PROMETHEE itself is considered a pre-treatment method for GAIA. These pre-treatment methods ensured that the patterns elucidated by the chosen chemometric techniques were true. The chemometric techniques applied to the data are described herein.

3.7.4 Principal Component Analysis (PCA)

Principal Component Analysis (PCA) is the most commonly used exploratory data analysis technique. PCA is one of the best statistical techniques for extracting linear relationships among a set of objects and variables. PCA involves data reduction and can be applied to any data matrix consisting of objects (such as water samples) and variables (such as trace elements and heavy metals). PCA has gained acceptance over other techniques due to its ability to handle large data sets and reduce the dimensionality to a manageable size while keeping as much of the original information as possible (Pinto et al., 2012). The original data are reduced through the formation of latent variables, or Principal Components (PCs), by linear combination of the original variables. The first Principal Component explains the largest amount of data variance; thereafter subsequent PCs account for decreasing

amounts of data variance, where the number of PCs cannot exceed the original number of variables.

One of the many advantages of chemometric techniques is that they are systematic, reproducible and amenable to visual display. The results of PCA are displayed by a scores plot, a loadings plot or a biplot. A scores plot exhibits the relationships between the objects while a loadings plot presents the relationships between the variables. A biplot is a combination of scores and loadings plots and displays the relationships between objects and variables. A biplot can be used to interpret where objects lie in relation to the variables. General information that can be obtained with the aid of a scores plot, loadings plot or biplot are as follows:

- Variables with high positive or high negative loadings are important (i.e. have a greater contribution); the longer the variable vector, the more important the variable is in positioning the objects.
- Objects close to each other are similar (resulting in cluster formation).
- Objects that appear in the same area as a variable vector are strongly related to that variable.
- Variable vectors that are at 90^{o} are not correlated, vectors at 180^{o} are in opposition and vectors travelling in the same direction provide similar information.

Comparisons in PCA can therefore be made variable to variable, object to object, or object to variable.

For this research, PCA was performed using SIMCA-P 10.0 software from Umetrics. A particular advantage associated with this software is that the Hotelling T2 95% confidence ellipse is displayed on every scores plot, allowing easy determination of outliers. Any object on a scores plot shown outside the ellipse was considered an outlier.

3.7.5 Hierarchical Cluster Analysis (HCA)

Cluster analysis is an unsupervised pattern recognition technique, designed to detect hidden groups in a set of objects, so that the members of each cluster behave similarly to each other and the groups are maximally separated (Xu et al., 2012). The overall aim of cluster analysis is to achieve a set of clusters in which the objects included in the same

cluster are similar to each other and different from the other objects belonging to other clusters (Manly, 1994), (Vieira et al., 2012).

Different clustering methods will yield similar results for robust, well separated clusters, but different results for clusters that overlap. Hierarchical Cluster Analysis (HCA) is the more popular method, and was performed for this research using Minitab 16 Statistical Software. HCA can be thought of as viewing objects as points in space, whereby every object in space is compared to all remaining objects to obtain a distance matrix. Therefore, objects with the shortest distance are aggregated, forming a new 'object' to which the remaining objects are compared and so on. Therefore, at each step, the most similar pair of objects is identified until all objects have been linked. A dendrogram is usually used to represent clustering information as the step by step linkage is most easily visualised with this 'tree diagram'.

Cluster analysis may be considered a better approach than other techniques, such as PCA, because it identifies the underlying factor in data without the need for any pre-assumption or a null hypothesis, and no simplification of data is required (Kumari et al., 2012). As a result, PCA and HCA are often used in tandem because they complement each other.

3.7.6 Multicriteria Decision Making (MCDM) Methods – PROMETHEE and GAIA

Multicriteria Decision Making (MCDM) methods are very powerful, real world tools. MCDM methods are capable of taking on many different criteria, achieving useful, practical and compromise solutions for decision makers. They are therefore a frequently employed experimental platform for rapid, visually effective modelling and testing of competitive scenarios.

Multicriteria Decision Making methods PROMETHEE (Preference Ranking Organisation METHod for Enrichment Evaluations) and GAIA (Graphical Analysis for Interactive Assistance) are widely considered to be two of the most popular decision making methods and are fast becoming the methods of choice for environmental studies. These non-parametric ranking methods facilitate the ordering of a number of objects according to preference and weighting conditions that have been pre-selected by the user and applied to variables (Ayoko et al., 2007). A significant advantage of PROMETHEE is that no pre-treatment is required. PROMETHEE itself serves as a data pre-treatment method for

GAIA, and provides both ranking and pattern recognition information. Another advantage is that each variable can be modelled and optimised separately, ideal for situations where alternative maximum and minimal values may be optimal.

PROMETHEE and GAIA were employed to gain an understanding of yearly data and to consider changing climatic conditions. The geometric mean concentrations of all trace elements and heavy metals (for each tuning step) for yearly potable water samples were used. In Decision Lab 2000 software, years (objects) were referred to as actions, and all elements and tuning steps (variables) were known as criterion. The preferential ranking of raw water sources in the greater Brisbane area was also achieved with PROMETHEE and GAIA. Similarly, all raw water sources (objects) were referred to as actions, and all elements and tuning steps were again known as criterion (variables) in Decision Lab 2000. The six preference functions available for PROMETHEE include usual, level, U-shape, V-shape, linear and Gaussian. The preference function chosen for this research was V-shape because it has been widely applied to environmental work. Environmental research conducted by Khalil et al. (2004), Lim et al. (2005), Friend and Ayoko (2009), and Crilley (2013), demonstrate that the V-shape preference function offers the best outcome. Additionally, the minimum (rather than maximum) variable modelling option was selected for the concentrations of trace elements and heavy metals in a sample. The minimum value is preferred for the criterion due to the reasonable assumption that the years and water sources (the objects or actions) with minimal trace element and heavy metal contamination would be the most preferred.

The ranking of yearly and raw water data was then facilitated by pair wise comparisons of the actions against the criteria using the maximum guideline values from the 2011 Australian Drinking Water Guidelines (ADWG), and the Australian and New Zealand Environmental and Conservation Council/Agricultural and Resource Management Council of Australia and New Zealand (ANZECC/ARMCANZ, 2000) water quality guidelines for toxicants respectively, as the threshold values. The ranking results were represented by preference flow values. Phi + ($\phi+$) is the positive flow which measures how much an action is preferred over other actions. The negative flow, phi - ($\phi-$), measures how much other actions were preferred to an action. The balance between these positive and negative preference flows is phi (ϕ), the net outranking flow, where the strength ($\phi+$) and weakness ($\phi-$) of the action is taken as a single value. As a result, ϕ can be positive or negative, where the larger (positive) ϕ value represents the better action. The criterions (or variables) were optimised to comply with the 2011 ADWG and the ANZECC/ARMCANZ (2000) water quality guidelines

for toxicants, that is, the maximum acceptable concentration of trace elements and heavy metals allowable in potable and raw water. As a result, the years and raw water sources tested (the objects in this research) were preferentially ranked in order of most complete compliance with the 2011 ADWG and ANZECC/ARMCANZ (2000) water quality guidelines for toxicants respectively, based on the concentrations of trace elements and heavy metals present.

Two types of ranking outcomes are achievable with PROMETHEE. PROMETHEE I is a partial ranking order and can have three possible outcomes, where one object is preferred to another, there is no difference between the two objects or the objects cannot be compared (Ayoko et al., 2003). Alternatively, PROMETHEE II is a complete ranking order wherein objects are forced into order. Although PROMETHEE II appears to be more efficient at ranking objects, it is less informative than PROMETHEE I which is usually considered better as a partial ranking is closer to the truth (Ayoko et al., 2004).

A visual interpretation of PROMETHEE results is GAIA, a special form of PCA. Only the first two PCs, representing the most variance in the data, are displayed. Dimensionless axes are used for segmentation of space in order to better present the strengths of the actions and criterions according to their position in the GAIA plane, positions also relevant to the *pi* (π) decision axis (Mladenovic-Ranisavljevic et al., 2012). The incorporation of the π decision axis reinforces the quality of the decision. Objects in the direction of the π decision axis can be perceived as the best decisions or options based on the criteria and preferences selected. If the π axis extending from the origin of the GAIA plane is long, there is said to be a lot of confidence in the decisions made. Alternatively, if the π axis is short, there is less confidence in the decision being made.

A GAIA plot can be interpreted similar to a PCA biplot, where the longer a variable vector is, the more important the variable. Variable vectors at 90^{o} are not correlated, vectors at 180^{o} are in opposition and vectors travelling in the same direction provide similar information, while objects that appear in the same area as a variable vector are strongly related to that variable.

3.7.7 Partial Least Squares (PLS) Analysis

Partial Least Squares (PLS) is a chemometric technique widely used to develop predictive models and is the most commonly used form of multivariate calibration. PLS was applied through SIMA-P 10.0 software in this research. This technique involves regression followed by prediction, and works with two matrices, **X** (e.g. predictors, factors, independent variables) and **Y** (e.g. responses or dependent variables) (Ayoko et al., 2007). The main objectives of this technique are to well approximate **X** and **Y**, and to model the relationship between them (Ayoko et al., 2007). The **X** matrix contains the predictors, while the **Y** matrix contains the responses. The variation in the predictor block, **X**, is summarised by the **X** scores (*T*), and the corresponding variation in the **Y** response block is described by the **Y** scores (*U*). PLS aims to maximise the covariance between *T* and *U* (Eriksson et al., 2001). In contrast, PCA models variance using only independent variables (X).

PLS attempts to find the least complex model that explains the data by relating **X** and **Y** to each other through regression. The data matrix achieved through the ICP-MS analysis of water samples in this research is a single matrix of one set of objects and variables, and does not fit the design required for PLS calibrations. As a result, the variables, the trace elements and heavy metals, were manually split into two groups, thus forming the **X** and **Y** blocks. Additionally, tap, tank and filtered water data from 2008 to 2012 were selected for use as the "work set", while tap, tank and filtered water data from 2013 was used as the "test set". Classes within the work and test sets were assigned based on water types.

The purpose of PLS analysis in this research is to model the work set to determine if historical data could be used as baseline data to accurately predict the concentrations of trace elements and heavy metals found in water samples analysed in 2013 and in the future. In this research, model validation is carried out by developing parallel models with randomly reordered data, otherwise known as response permutation. There are several other methods commonly used for model validation, such as cross-validation and external validation. This analysis and model development explores the possibility of using multivariate data analysis methods to predict water quality from a smaller number of easily measured variables, as previously performed by Ayoko et al. (2007).

3.8 Summary

The careful and combined application of all methodologies and techniques described in this chapter led to the successful analysis of numerous trace elements and heavy metals in raw and potable water samples. The manner in which these methods progressed and how they were intertwined is best summarised by the Input and Output Flow diagram in Figure 3-4. The following Chapter Four: Results and Discussion contains all results achieved by these quantitative, qualitative and statistical methodologies.

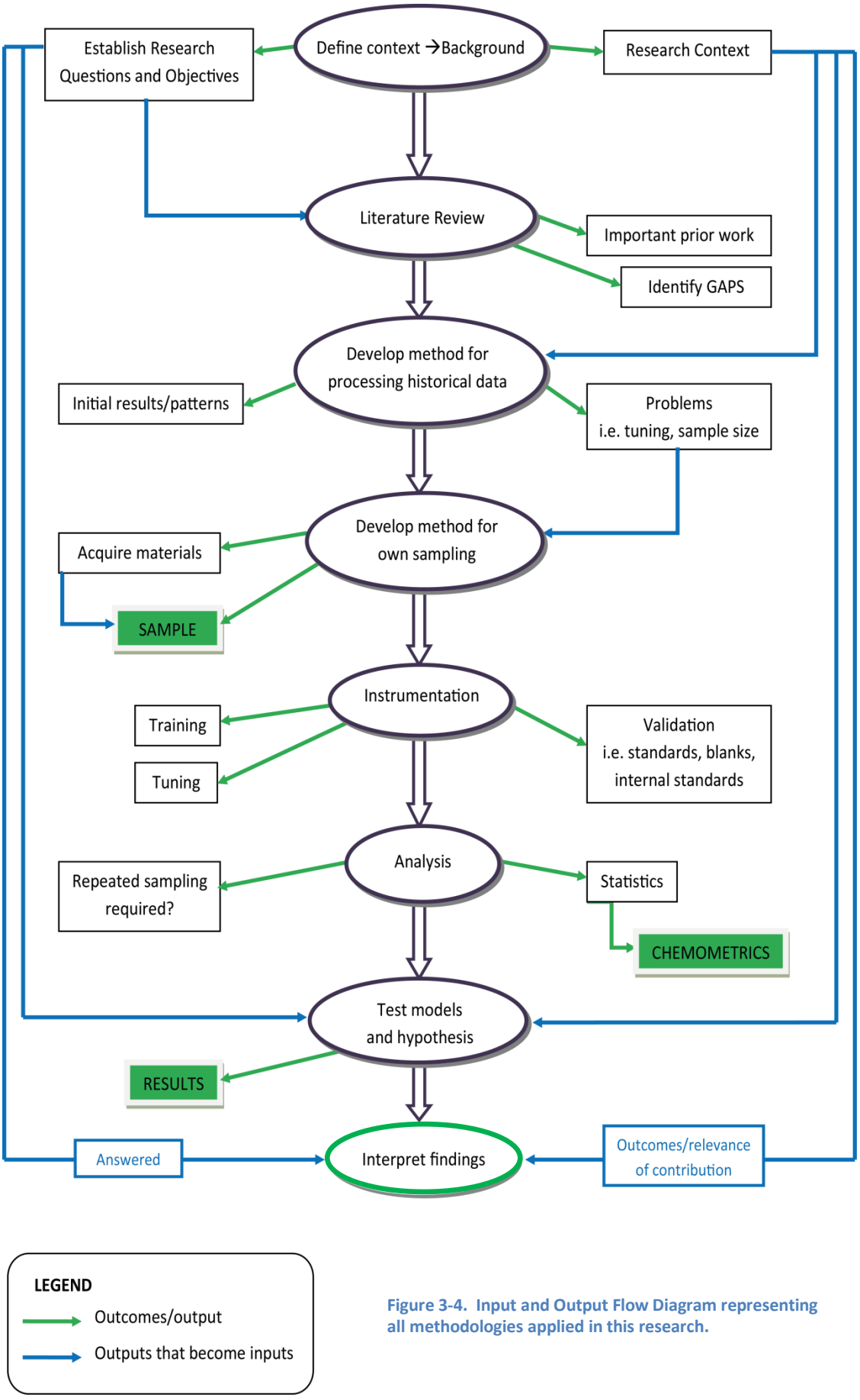


Figure 3-4. Input and Output Flow Diagram representing all methodologies applied in this research.

Chapter Four: Results and Discussion

This Results and Discussion chapter will systematically convey all results achieved through sample analysis via Inductively Coupled Plasma - Mass Spectrometry (ICP-MS), basic statistics and chemometrics. The analysis of all results will assess the implications, similarities, differences and connections to other areas of this research as well as the relevant literature. This chapter further investigates the theories devised from the analysis of results and deliver complete answers to the research questions and objectives proposed earlier in this thesis.

4.1 Longitudinal Study 2008 – 2012

This research involved obtaining data from original sample collection and ICP-MS analysis of 26 trace elements and heavy metals of interest for over 200 samples for the purpose of this research during 2013. Additionally, reanalysis of data collected by students at Queensland University of Technology from 2008 to 2012 was used to complete a longitudinal study of water quality. This historical data were collected as part of an undergraduate student practical performed over successive years with different student cohorts each year. The method used was based on the US EPA Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry. Students were supplied with 50 mL capped plastic centrifuge tubes for ICP-MS and tasked with the collection of tap, tank and filtered water from their homes, resulting in waters from a variation of post codes. Numerous brands of bottled water were also collected. This undergraduate practical continues to be performed at QUT.

4.1.1 Reanalysis of Historical Data for Longitudinal Study

Following ICP-MS and data analysis of samples collected in 2013 for this research, investigations determined that the historical data collected from 2008 to 2012 required extensive reanalysis to improve the accuracy of the results achieved, thereby enhancing the validity of these data. It was concluded that the ICP-MS instrument tuning between pulse counting mode and analog counting mode for signal collection was incorrectly calibrated, if at all, prior to analysis of samples from 2008 to 2012. As a result, the reanalysis of the historical data involved retrospective calibration to rectify this tuning error. The differences in methodology between historical data collection and current data collection highlighted the need for reanalysis via retrospective calibration of this historical data.

One of the main differences in the ICP-MS method used for the analysis of the 2013 samples was the additional use of a specific Pulse/Analog (PA) Tuning Solution that was not used in undergraduate practicals, while the Agilent Tuning Solution was used for the instrument across all six years. A PA Factor tuning solution is recommended in the Agilent 7500 ICP-MS ChemStation Operator's Manual (Agilent Technologies Inc., 2005a). The additional use of the PA Tuning Solution and subsequent results uncovered anomalies in the calibration (or tuning) between the pulse and analog count signals in the historical data

(collected from 2008 to 2012). Initial investigations of the Agilent Environmental Calibration Standard concentration results as a whole revealed that the calibration between pulse and analog counts collected via ICP-MS was unsuccessful over all five years of historical data.

An example of the Agilent Environmental Calibration Standard results collected for ^{9}Be in 2013 is shown in Figure 4-1. The PA Tuning Solution was used for the collection of this data, and as such, accurate calibration between the two detection modes was achieved.

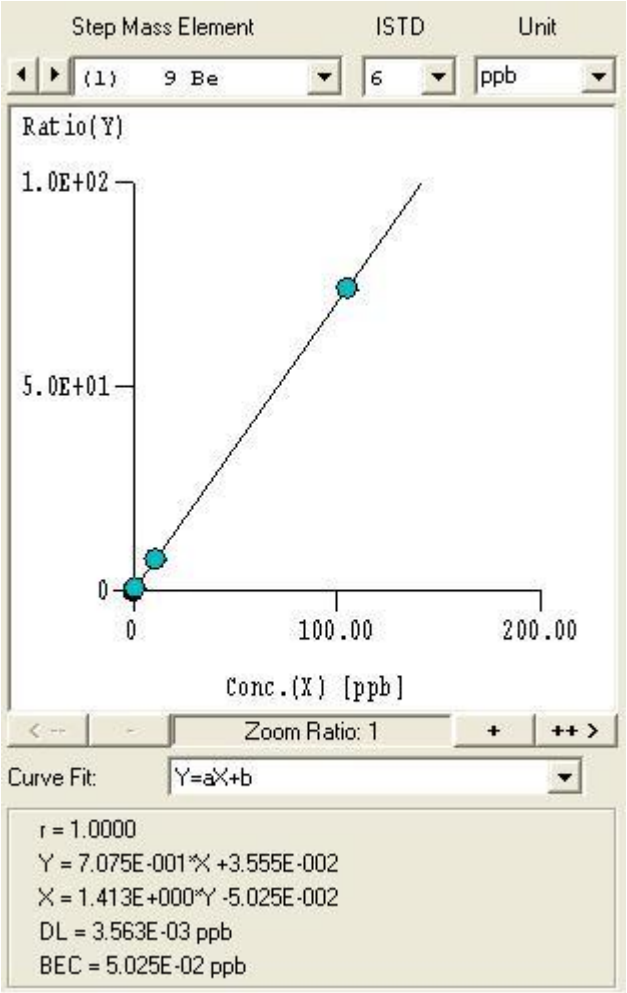


Figure 4-1. Calibration plot of Concentration (µg/L) vs. Counts for ^{9}Be in each standard for batch Kate17ja collected in 2013, as seen in Agilent ChemStation software. The correlation coefficient and equation for line of best fit are also shown. Blue data points denote pulse counts.

Figure 4-1 demonstrates good correlation (R^2 = 1.0000) between all pulse counting points collected. It is important to note that the detector will automatically switch between pulse and analog counting modes when necessary. Pulse counting mode covers the range from sub ng/L (ppt) to 100 µg/L (ppb); above this, hundreds of mg/L (ppm) is the range covered

by the analog counting mode (Agilent Technologies Inc., 2005a). Because the highest concentration of the calibration standard solutions for beryllium does not exceed 100 µg/L, pulse counting mode was used to collect all signal data for this element.

On the basis of the current 2013 data attained with the use of the PA Tuning solution, the results collated from the historical data were re-examined. When historical and current data were compared, it was determined that the use of the PA Tuning Solution for sample analysis was an advantageous addition to the ICP-MS method because of the greater accuracy of the results achieved.

The Agilent PA Tuning solution is a relatively new and expensive product (introduced in 2007), and was considered an unnecessary luxury for use in undergraduate practical sessions. Although PA tuning can still be accomplished with the standard instrument tuning solution when setting up the instrument, it is inferred from revisiting the historical data that the tuning for the pulse/analog counting, if performed, was unsuccessful.

The results from the Agilent Environmental Calibration Standard solutions for ^{9}Be, the same example element shown in Figure 4-1, are used as an example from historical student data collected in 2012. This data was collected without the use of a PA Tuning Solution. These results, shown in Figure 4-2, demonstrate that the correlation coefficient is lower in comparison to the same element analysed in 2013. Switching from pulse to analog counting mode also occurs despite the concentration of the standard solutions not exceeding 100 µg/L.

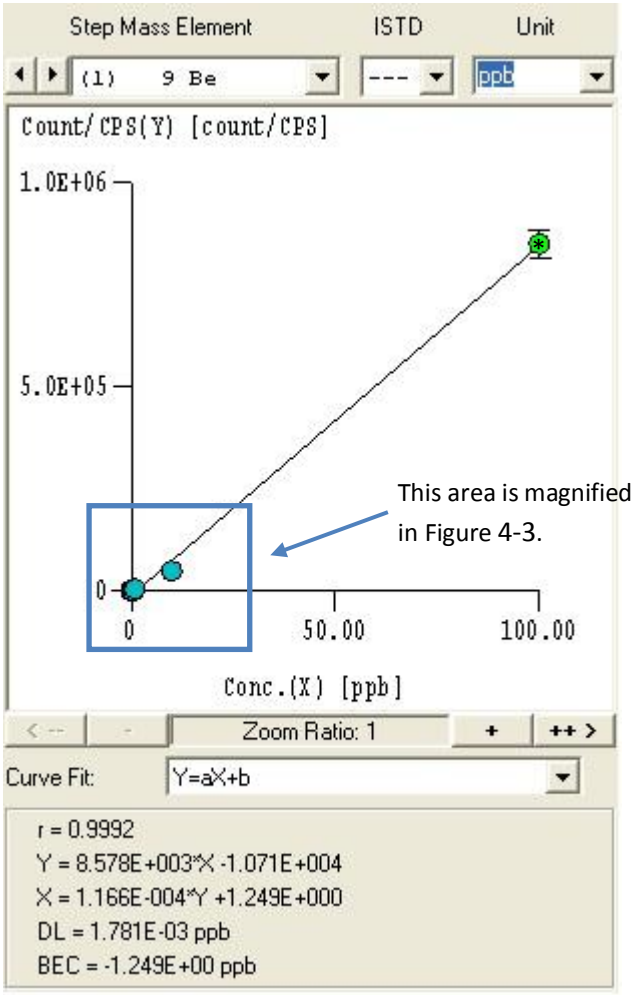


Figure 4-2. Calibration plot of Concentration (µg/L) vs. Counts for ^{9}Be in each standard for batch 150512TU collected in 2012, as seen in Agilent ChemStation software. The correlation coefficient and equation for line of best fit are also shown. Blue and green (with star) data points denote pulse and analog counts respectively.

Figure 4-2 demonstrates a good correlation (R^2 = 0.9992) between the pulse and analog counting points collected. Based on Figure 4-2, the concentration of ^{9}Be calibration standard 4 recorded for of this batch must be greater than 100 µg/L, and so the detector collected this point in analog counting mode. Despite a correlation coefficient of 0.9992 generally indicating good correlation, Figure 4-3, a magnification of Figure 4-2, shows a poor line of best fit between the pulse counting points collected when the analog counting signal is included.

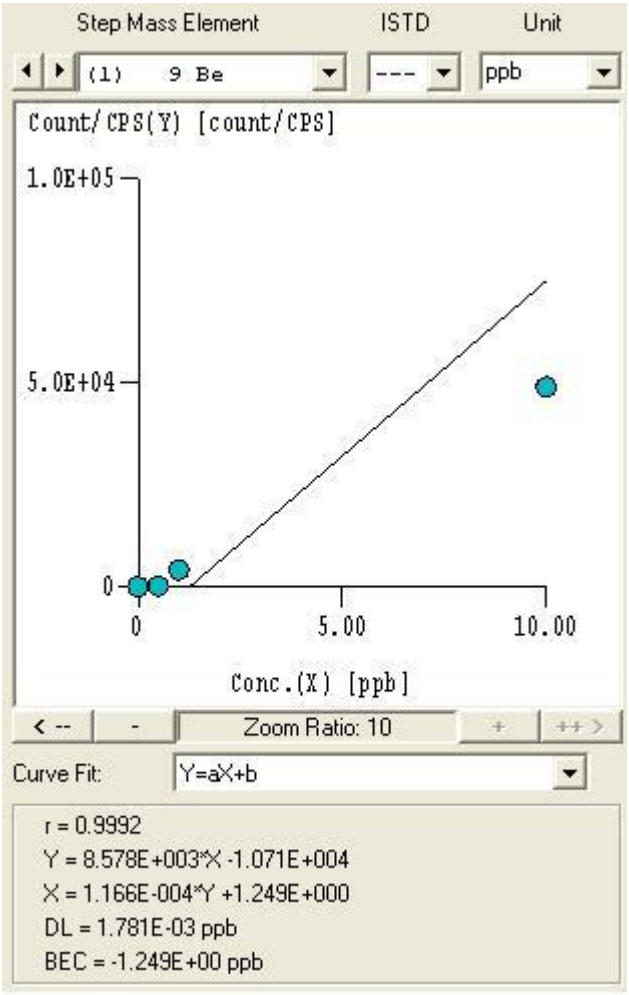


Figure 4-3. Magnification of the calibration plot as seen in Figure 4-2.

This same result was observed in many of the standard calibration plots that had low R^2 values. Therefore, the hypothesis developed to account for these observations was that the calibration between the pulse and analog counting modes was unsuccessful for years 2008 to 2012. In order to rectify this unsuccessful calibration, a retrospective pulse/analog calibration was performed on all historical data. This retrospective calibration was accomplished using Agilent ChemStation software and Microsoft Excel, whereby all concentration data was exported through FileView32.

The retrospective calibration involved determining a pulse/analog (P/A) ratio for each element. This ratio was based on the slopes of the standard calibration curves as seen in Agilent ChemStation. The process involved three main steps:

1. To find the slope of the (blue) pulse counts by removing all (green) analog counts.
    - Individual points can be turned “OFF” in Agilent ChemStation.

2. Similarly, to find the slope of the (green) analog counts by removing all (blue) pulse counts.
    - If there was only one analog point, the blank pulse count was left "ON" to find the analog slope (and vice versa).
3. Mixed signals were generally removed when slopes were determined.

Once individual pulse and analog slopes were extracted, the pulse/analog (P/A) ratio for each element was found and applied to all analog points for that element. There were more pulse points than analog points, therefore this approach minimised the process.

An example of this process is again shown for ^{9}Be from batch 150512TU (data collected May 15, 2012 – Tuesday Group). The original standard calibration curves for this element were previously seen in Figure 4-2 and Figure 4-3.

Table 4-1. Counts per Second (CPS) values, calibration plot slopes for both pulse and analog counts, and the application of (rounded) P/A ratio for ^{9}Be [#1].

	^{9}Be [#1] (CPS)	Count Signal
Pulse slope	4991	
Analog slope	8496	
P/A Ratio	0.5875	
Blank (0 µg/L)	5.56	Pulse
Standard 1 (0.5 µg/L)	197.79	Pulse
Standard 2 (1 µg/L)	4156.31	Pulse
Standard 3 (10 µg/L)	48927.25	Pulse
Standard 4 (100 µg/L)	849607.6	Analog

$$\frac{Pulse\ slope}{Analog\ slope} = P/A\ Ratio$$

$$E.g.: \frac{4991}{8946} = 0.5875$$

$$Correction\ applied\ to\ Analog\ count:$$
$$\therefore\ 849607.6 \times 0.5875 = 499104.465$$

This process was completed for each element under each tuning condition: [#1], [#2] and/or [#3], hydrogen gas, helium gas and no gas respectively, for all standards (including the blank). Consequently, all standard calibration curves were recreated with the adjusted analog points. As a result, the new calibration plot displayed in Figure 4-4 for ^{9}Be [#1] was constructed with the blank and standard values shown in Table 4-2. For this element, the counts per second (CPS) were only adjusted for Standard 4, the only standard CPS collected as an analog signal, highlighted (purple) in Table 4-2.

Table 4-2. Altered Count per Second (CPS) values for ^{9}Be [#1] following the determination of the Pulse/Analog Ratio.

	^{9}Be [#1] (CPS)	Count Signal
Pulse slope	4991	
Analog slope	8946	
P/A Ratio	0.5875	
Blank (0 µg/L)	5.56	Pulse
Standard 1 (0.5 µg/L)	197.79	Pulse
Standard 2 (1 µg/L)	4156.31	Pulse
Standard 3 (10 µg/L)	48927.25	Pulse
Standard 4 (100 µg/L)	499104.465	Analog

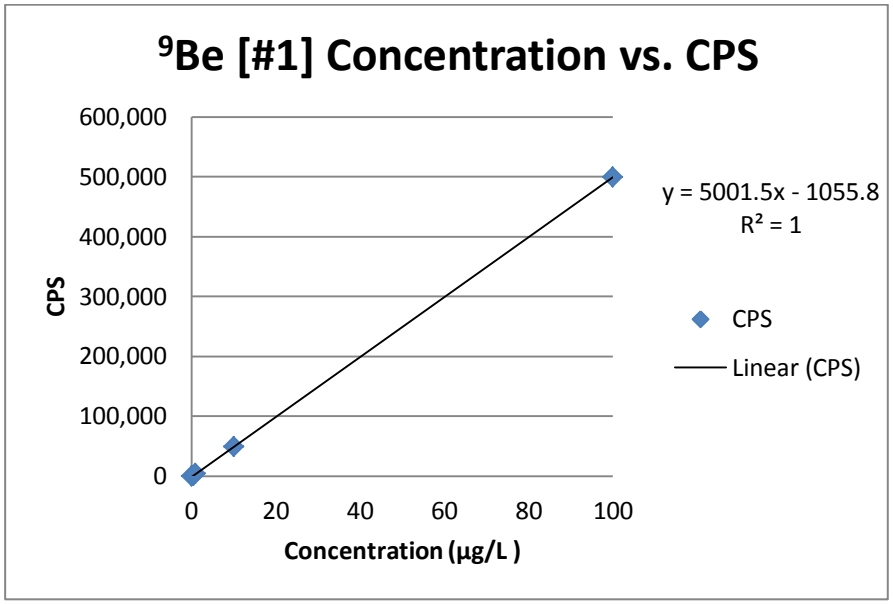


Figure 4-4. Recreated calibration plot depicting the standard concentrations in parts per billion (µg/L), and Counts per Second in which the pulse and analog signals were collected. The correlation coefficient and equation for line of best fit are also shown.

In contrast to Figure 4-2 and Figure 4-3, the recreated standard calibration curve that is Figure 4-4 shows a significantly improved correlation coefficient of $R^2 = 1$. This improvement verifies the proposed hypothesis and shows that the retrospective calibration process is justified. This method was therefore used on all historical data to correct the unsuccessful pulse/analog calibration for these years. Consequently, the unknown sample concentrations were recalculated from the new standard calibration curves for each element under each tuning condition.

Exceptions to this process were encountered when, as is exampled by ^{23}Na [#1] of the same batch (150512TU) (shown in Table 4-3), the blank (0 µg/L) counts per second, collected as an analog signal, were higher than the Standard 1 (50 µg/L concentration) counts per second, collected as a pulse signal. In order to determine the pulse slope for this element, the singular pulse count collected (standard 1) was used with the 10,000 µg/L analog signal (standard 4), instead of the blank analog signal. This was done to prevent a negative pulse slope and consequently a negative slope in the new standard calibration curve. This approach deviates from the devised method, which states that the blank count signal is to be used in a situation where only one pulse or analog count signal was recorded amongst the five signals (blank, and standards 1 – 4) collected.

Table 4-3. The original and P/A ratio corrected CPS data for ^{23}Na [#1].

Original	^{23}Na [#1] (CPS)	Count Signal
Pulse slope	6718	
Analog slope	6616	
P/A Ratio	1.0154	
Blank (0 µg/L)	1287420	Analog
Standard 1 (50 µg/L)	269346.2	Pulse
Standard 2 (100 µg/L)	1118301	Analog
Standard 3 (1000 µg/L)	7784549	Analog
Standard 4 (10000 µg/L)	67109090	Analog

Corrected	^{23}Na [#1] (CPS)	Count Signal
Pulse slope	6718	
Analog slope	6616	
P/A Ratio	1.0154	
Blank (0 µg/L)	1307268.37	Analog
Standard 1 (50 µg/L)	269346.2	Pulse
Standard 2 (100 µg/L)	1135542.04	Analog
Standard 3 (1000 µg/L)	7904564.72	Analog
Standard 4 (10000 µg/L)	68143722.3	Analog

The successful retrospective calibration of all five years of historical data resulted in far more accurate correlation coefficients for standard calibration curves, generally greater than 0.9995, and hence more accurate sample concentrations. Concurrently, the result of completing this retrospective calibration process clearly demonstrated that the use of the PA Tuning Solution for ICP-MS data collection in 2013 successfully calibrated the pulse and

analog counting signals prior to data collection. Therefore, the complementary use of the PA and Agilent Tuning Solutions was necessary and successful, with the correlation coefficients seen to be much closer to or indeed $R^2 = 1.0000$. Additionally, the relative standard deviations (RSDs) returned were significantly smaller than results from previous years.

Following the retrospective calibration process, minimal pre-treatment was performed prior to comparing the raw concentration data from 2008 to 2012 directly to the 2011 Australian Drinking Water Guidelines (ADWG).

4.1.2 Treatment of Missing and Negative Values in Historical Data

Depending on the individual student cohort, four to six batches of water samples were collected and analysed each year from 2008 to 2012. Following the retrospective calibration and recalculation of all sample concentrations, basic statistics were applied to what was now accurate raw data. Basic statistical information included the mean, geometric mean, range and standard deviation. Additionally, the number of missing values was determined, where missing values eventuated from batch data being combined and analysed in yearly batches. As there were four to six batches of samples collected and analysed via ICP-MS per year, there were occasional instances where additional elements, different isotopes and/or varying tuning steps were collected in the separate analytical runs, resulting in differences across the batches. These missing values were replaced with the geometric mean of the column, as is the convention for environmental data. This procedure is also exampled in previous work by colleagues Adrian Friend (Friend, 2012) and Leigh Crilley (Crilley, 2013).

Prior to the correction for the PA Factor tuning as described in section 4.1.1, Agilent ChemStation software returned many negative concentrations for elements at low concentrations. As seen in Figure 4-3, the miss-calibration of the PA Factor tuning often lead to a negative intercept. As a result, calculations for low concentrations made with the standard calibration model were misrepresented as negative concentrations. The corrections described in section 4.1.1 improved the frequency of this occurrence; however, it can be inferred that concentrations close to the detection limit were incorrectly displayed as negative values, in addition to the concentrations genuinely below the detection limit. Consequently, half of the Method Detection Limit (MDL) concentration for each variable

was used to replace any negative values. The MDL was determined to be one third of the lowest positive concentration returned for each variable. The process of replacing negative values with half the MDL is based on the physical reality that the contaminant contributions of trace elements and heavy metals in the environment cannot be negative (Rachdawong & Christensen, 1997).

4.1.3 Raw Data Analysis of Historical Data

Following this treatment of missing and negative values and prior to employing any chemometric techniques, the yearly raw data collected from 2008 to 2012 was directly compared to the 2011 Australian Drinking Water Guidelines (ADWG) to determine if the potable water samples tested were within the aesthetic and health limits. As all sample concentrations were collected in µg/L, Table 4-4 is a reiteration of Table 1-2 from Chapter One, with the relevant guideline values converted from mg/L to µg/L.

Table 4-4. Guideline values of trace elements and heavy metals of interest, taken from *Table 10.5 - Guideline values for physical and chemical characteristics in 2011 ADWG*. c denotes "Insufficient data to set a guideline value based on health considerations" (National Health and Medical Research Council, 2011). The right-hand column (orange) lists the concentrations of elements of interest in µg/L.

Characteristic	Guideline values (mg/L)		Comments	Guideline values (µg/L) *(Aesthetic guideline preferable)*
	Health	Aesthetic		
Aluminium (acid-soluble)	c	0.2	Guideline value based on post-flocculation problems; <0.1 mg/L desirable. Lower levels needed for renal dialysis. No health based guideline value can be established currently.	200
Antimony	0.003		Exposure may rise with increasing use of antimony-tin solder.	3
Arsenic	0.01		From natural sources and mining/industrial/agricultural wastes.	10
Barium	2		Primarily from natural sources.	2000
Beryllium	0.06		From weathering rocks, atmospheric deposition (burning fossil fuels) discharges.	60
Cadmium	0.002		Indicates industrial or agricultural contamination; from impurities in galvanised (zinc) fittings, solders and brasses.	2
Chromium (as Cr(VI))	0.05		From industrial/agricultural contamination of raw water or corrosion of materials in distribution system/plumbing. If guideline value exceeded, analyse for hexavalent chromium.	50
Copper	2	1	From corrosion of pipes/fittings by salt, low pH water. Taste threshold 3 mg/L. High concentrations colour water blue/green. >1 mg/L may stain fittings. >2 mg/L can cause ill effects in some people.	1000
Iron	c	0.3	Occurs naturally in water, usually at <1 mg/L, but up to 100 mg/L in oxygen-depleted groundwater. Taste threshold 0.3 mg/L. High concentrations stain laundry and fittings. Iron bacteria cause blockages, taste/odour, corrosion.	300
Lead	0.01		Occurs in water via dissolution from natural sources or household plumbing containing lead (e.g. pipes, solders).	10
Manganese	0.5	0.1	Occurs naturally in water; low in surface water, higher in oxygen-depleted water (e.g. groundwater at bottom of deep storages). >0.1 mg/L causes taste, staining. <0.05 mg/L desirable.	100
Mercury	0.001		From industrial emissions/spills. Very low concentrations occur naturally. Organic forms most toxic, but these are associated with biota, not water.	1
Molybdenum	0.05		Concentrations usually <0.01 mg/L; higher concentrations from mining, agriculture or fly-ash deposits from coal-fuelled power stations.	50
Nickel	0.02		Concentrations usually very low; but up to 0.5 mg/L reported after prolonged contact of water with nickel-plated fittings.	20
Selenium	0.01		Generally very low concentrations in natural water.	10
Silver	0.1		Concentrations generally very low. Silver and silver salts occasionally used for disinfection.	100
Sodium	Not necessary	180	Natural component of water. Guideline value is taste threshold.	180,000
Uranium	0.017		Occurs naturally, or from release of mill tailings, combustion of coal and phosphate fertilizers.	17
Zinc	c	3	Usually from corrosion of galvanised pipes/fittings and brasses. Natural concentrations generally <0.01 mg/L. Taste problems > 3mg/L.	3000

4.1.3.1 2008 Raw Data

The vast majority of water samples collected in 2008 complied with the 2011 ADWG. The sample concentrations returned for mercury (^{202}Hg) were considered anomalous as they were all significantly greater than the health guideline value of 1 µg/L, with the exception of the concentrations that were originally negative and subsequently replaced with half the MDL concentration. The conclusion that these results are anomalous is valid as previous literature has shown that the use of only nitric acid to preserve water samples, as was the case for this research, produces erroneous results for mercury, and a mixture of both nitric and hydrochloric acid is recommended for the preservation of mercury (Louie et al., 2012).

In total, there were nine samples where iron concentrations were observed in excess of the 300 µg/L aesthetic guideline, however, there is no health guideline set for this element, and as iron is a vital element for human health, the higher concentrations recorded here are not believed to be concerning. One of these nine samples also exceeded the aesthetic guideline (but not the health guideline) for manganese, as well as the health guideline for lead. The high concentrations of elements iron and lead that surpass the guidelines in this tank water sample (08C1K00S1050) from Woolloongabba indicate that the roof from which the water flowed into the tank where this sample was collected, may have lead and/or steel nails or downpipes, lead flashing, galvanised iron or other steel roofing materials; or lead-based solder may have been used for pipe joints. It is known that lead is used in roofing nails and washers (Block, 2009). According to enHealth (2011), roof materials and uncoated lead flashing remain a potential source of contamination. The problem can be greater due to poorly maintained roofs and gutters, where the water is made more acidic with organic substances from materials such as leaf litter. Similarly, rain water itself tends to be more acidic; these factors mobilise lead, and possibly other metals, into solution (Environmental Health Committee (enHealth), 2011).

4.1.3.2 2009 Raw Data

Again in 2009, samples collected mostly complied with the 2011 ADWG. The sample concentrations returned for mercury (^{202}Hg) were again considered anomalous as explained in section 4.1.3.1, exceeding the health guideline value of 1 µg/L, except for the concentrations that were originally negative and replaced with half the MDL concentration.

Of all the samples analysed in this year, 16 samples showed iron concentrations greater than the aesthetic guideline of 300 µg/L, although no health guideline is imposed for this element. Similarly, one water sample exceeded the aesthetic guideline for copper, but was well under the health guideline of 2000 µg/L. Three samples, one tank and two tap water, exceeded the health guideline of 20 µg/L for nickel, and one of these tap water samples (514Fri13S2111) as well as an additional tank water sample also exceeded the health guideline of 10 µg/L for lead.

The presence of nickel is most likely due to household plumbing fixtures that contain or are plated with nickel, like faucets; additionally, metal alloys used for roofing materials may also contain amounts of nickel that can be washed into solution, as described by enHealth (2011) in section 4.1.3.1. The high lead levels in the tank water sample can be attributed to roofing materials used (Environmental Health Committee (enHealth), 2011), as previously described for the data collected in 2008. Elevated concentrations of lead in tap water, as seen here, may be attributed to the use of lead solder for copper pipe joins and/or copper and brass faucet joints (Block, 2009). Block (2009) reported that experts regard the corrosion of lead solder as the major cause of lead contamination in drinking water today. The use of lead-based solder has been banned in Australia since 1989 (The Lead Group Inc., 2013). Lead piping was popular in household plumbing systems until early in the 20th century, therefore, homes built prior to the 1930s are likely to contain lead piping (PropEx Services LLC, 2002-2005). This is not believed to be the case for this sample (514Fri13S2111) as the health guideline is exceeded by less than 4 µg/L.

4.1.3.3 2010 Raw Data

Every sample collected and analysed in 2010 conformed to the 2011 ADWG. Two samples, one bottled water and one tap water, had concentrations of iron that exceeded the aesthetic guideline for this element, but adverse health effects are not a concern at the concentrations observed.

4.1.3.4 2011 Raw Data

A variety of the samples collected and analysed in 2011 did not conform to the 2011 ADWG. One sample exceeded manganese concentrations for the aesthetic guideline (100 µg/L) but not the health guideline (500 µg/L). All but two samples had iron concentrations in significant excess of the 300 µg/L aesthetic guideline. Additionally, a 10 µg/L excess above the 20 µg/L nickel health guideline was observed in two tap water samples. As described for data collected in 2009, these high nickel concentrations are most likely attributable to household plumbing materials and fixtures containing nickel, such as washers and faucets. Ten samples surpassed both the aesthetic and health guidelines imposed for copper, which are 1000 and 2000 µg/L respectively, with some concentrations reaching almost 20,000 µg/L. Such high copper levels infer that the samples collected were from homes built prior to the late 1980s, when copper pipes were prominently used for plumbing (PropEx Services LLC, 2002-2005). It is also not uncommon for many newer houses to still use copper pipes for the hot water system, and PVC pipes for sewage and grey water.

4.1.3.4.1 Tap Water

Seven tap water samples have zinc concentrations significantly higher than the aesthetic guideline of 3000 µg/L for this element. However, there is no health guideline for zinc, and it can be inferred that excess zinc is an indicator of galvanised pipes and fittings in the homes from which these samples were collected. Galvanised pipes and fittings are made from steel or iron and are coated with zinc. They were commonly used in homes built prior to the mid-1960s (Gosford City Council, 2014). Furthermore, brass, an alloy composed of copper and zinc, has many uses including pipes, faucets, valves and other fittings (Block, 2009), all of which could contribute to the excess levels of zinc in these water samples.

It was also considered unusual for a single tap water sample to report a concentration greater than 100 µg/L for silver. It is possible that silver may be present in copper and nickel alloys (Lenntech BV, 2012). Lastly, five tap water samples contained concentrations higher than the 10 µg/L health guideline for lead. These elevated lead levels may be explained by the use of lead-based solder for copper pipe joins and/or copper and brass faucet joints (Block, 2009). As demonstrated for the data collected in 2009, the corrosion of lead-based solder, banned from use in Australia since 1989, is considered by experts to be the primary source of lead in drinking water (Block, 2009). Additionally, copper fixtures, which are used in many homes, are known to have small amounts of lead in their

casting (PropEx Services LLC, 2002-2005). Therefore, there are several sources of lead in the home that can each be considered as a source of contamination in tap water.

4.1.3.4.2 Bottled Water

Two samples, both identified as the Fiji brand of bottled water, had almost double the health guideline concentration of 10 µg/L for arsenic. Five samples (four of which were bottled water) just exceeded the health guideline of 10 µg/L in place for selenium. An evian® bottled water sample exceeded the health guideline of uranium, which is 17 µg/L. Finally, four bottled water samples from evian® and Fiji respectively contained concentrations double and quadruple that of the health guideline of 3 µg/L for antimony. It is believed that these unusual results of the analysis of these bottled water samples are because the same bottled water samples were used week after week for students of this yearly cohort. As a result, it is possible that the age of these samples had an effect on element concentrations, or that prolonged exposure leached trace amounts of this metal from the containers in which the samples were stored. Previous research by Westerhoff et al. (2008) concluded that antimony can be released from the PET plastic used to make commercial water bottles, and Krachler and Shotyk (2009) confirmed that antimony levels found in bottled water in the course of their research were caused by leaching from the PET plastic, and did not reflect the natural abundance of antimony in the source waters.

4.1.3.5 2012 Raw Data

Of the samples collected in 2012, four samples surpassed the rather high aesthetic guideline of 180,000 µg/L for sodium, although there is no health guideline in place for this macroelement. The WHO (2003) state that sodium salts, found in all types of drinking water, may affect taste at levels above 200,000 µg/L. All four samples exceeded this threshold, with concentrations of sodium ranging from 219,000 µg/L to 378,000 µg/L. Consumer comments, if any, were not recorded with sample collection for the undergraduate practical, so it is not known if the residents who supplied these water samples complained of salty drinking water. However, it may be inferred that not all of the sodium ion content detected in these water samples could be attributed to sodium chloride, or salt, and that the sodium ions may have formed many other compounds that did not have an effect on taste.

Similarly, the aesthetic guideline of 200 µg/L for aluminium was exceeded by just one tap water sample. A total of 12 tap, four bottled, three filtered and one tank water sample also exceeded the aesthetic guideline of 300 µg/L for iron, where these high concentrations can most likely be attributed to natural sources as well as galvanised pipes or fittings. Galvanised pipes and fittings are steel or iron coated with zinc, and can corrode with age, forming oxidised iron (rust) within the pipe or on fittings (Gosford City Council, 2014). It is common for homes built throughout the 1950s and 1960s to have galvanised pipes, and galvanised fittings are still in use today.

One tap water sample exceeded the health guideline for nickel (20 µg/L), while two samples exceed the aesthetic guideline for copper, but not the health guideline of 2000 µg/L. As previously stated, nickel may enter water from fixtures containing or plated with nickel, such as water faucets. Similarly, copper pipes and copper-containing fixtures are commonplace in many households, particularly those built before the late 1980s (PropEx Services LLC, 2002-2005), so it is plausible that excess copper and nickel is due to the composition of household plumbing.

One tap water sample from Boondall (150512TUSAMPLE3) showed concentrations more than double the health guideline of 10 µg/L for arsenic. Nine different tap, tank and filtered water samples had concentrations significantly exceeding the 10 µg/L health guideline for selenium. A single sample possessed more than ten times the amount of antimony, with the health guideline at only 3 µg/L. Finally, one tank water sample just exceeded the health guideline of 10 µg/L for lead. This elevated lead concentration may be explained in the same way as previous tank water samples, where roofing materials at this home may have included lead nails or downpipes, lead flashing, or lead-based solder used for pipe joints. As demonstrated for data collected in 2008, lead is used in roofing nails and washers (Block, 2009), with roof materials and uncoated lead flashing also posing a potential source of contamination. Water that is acidic can mobilise lead, and possibly other metals, into solution (Environmental Health Committee (enHealth), 2011).

4.1.3.6 Conclusions from Raw Data Analysis of Historical Data

These initial observations of the raw data collected from 2008 to 2012 demonstrate that overall, the water samples collected conformed to the 2011 Australian Drinking Water Guidelines. There were consistently high but not adverse levels of iron in drinking water

from the greater Brisbane area, as well as significant levels of copper and zinc, and occasionally lead and nickel, across all five years tested. These observations allow the inference that the water distribution system, household plumbing systems and roofs (from which tank water runs off) all make use of galvanised steel or iron pipes coated in zinc, copper pipes, as well as lead-based solders, lead nails, lead flashing and nickel plating or nickel-containing (brass) fixtures, as evidenced in this analysis. Beyond basic statistics, these simple conclusions are the extent of information that can be drawn from the analysis of the water samples collected. This limited insight into the huge quantity of data necessitates the use of chemometrics to extract the most information and form significant and discerning conclusions.

4.1.4 Data Pre-treatment and Chemometric Analysis of Historical Data

All data should be pre-treated prior to the application of chemometrics. There are numerous options available to prepare the data for multivariate statistical techniques. The most basic pre-treatment was completed in the process of determining basic statistics, whereby all missing or negative values were replaced. Subsequently, the most relevant pre-treatment methods for the particular chemometric techniques chosen were automatically applied to the data matrix by the software utilised for this research.

In the data matrix for this research, all water samples are considered objects. Similarly, all tuning steps for all trace element and heavy metal isotopes analysed are included as individual variables in all chemometric techniques. The tuning steps recorded were [#1] hydrogen (reaction) gas, [#2] helium (collision) gas and [#3] no gas. As a result, there are three concentrations for each trace element and heavy metal isotope analysed, and all are considered variables in this research.

Principal Component Analysis and Hierarchical Cluster Analysis were applied in tandem to maximise recognition of patterns in the yearly batches of pre-treated data. The software used for Principal Component Analysis (PCA) was SIMCA-P 10.0 (Umetrics AB, 2005a). Similarly, Minitab 16.0 (Minitab Inc., 2010) was used for Hierarchical Cluster Analysis (HCA).

Imported data was automatically auto-scaled, whereby a combination of mean-centring and standardisation ensures that each variable has equal weight. Auto-scaling produces data with zero mean and unit variance (standard deviation of 1) and is a method of choice

for multivariate analyses as shown in Chapter Two. Data variance is the basis of both PCA and HCA methods, therefore elements and/or tuning steps possessing little or no variance were removed from each data set. Additionally, the ellipse depicted on all PCA scores plots is the Hotelling T2 95% confidence ellipse, calculated by the Umetrics software SIMCA-P 10.0. Objects that fall outside the ellipse are considered outliers.

Prior to applying chemometric techniques, the expectation and hypothesis for the pooled historical data was that they would cluster according to potable water source, meaning discriminate clusters of tap, tank, filtered, bottled and reverse osmosis (2008 only) water would be observed. Principal Component Analysis (PCA) was the first chemometric technique to be applied to the historical data.

The hypothesised clustering of different sources of potable water was not verified by the results of the exploratory data analysis of the pooled yearly data. Emerging patterns can be observed in Figure 4-5, however, the distinction between different potable water sources is not clear. Therefore, further investigation was undertaken.

Instead of colouring samples according to the different sources of tap, tank, bottled, filtered and reverse osmosis water (2008 only) as seen in Figure 4-5, Figure 4-6 shows the same samples on the same PCA plot this time coloured according to the year in which each sample was collected.

Similarly, distinct clustering according to yearly batches was not observed in Figure 4-6. The vast majority of the 218 samples that were collected as part of this longitudinal study across years 2008 to 2012 are shown to possess a relatively small amount of variance. This is demonstrated by significant clustering around the origin of the PCA scores plot. Additionally, almost all samples are within the Hotelling T2 95% confidence ellipse, and only 10 samples lie outside of this ellipse, indicating that these samples (all collected in 2011) are outliers.

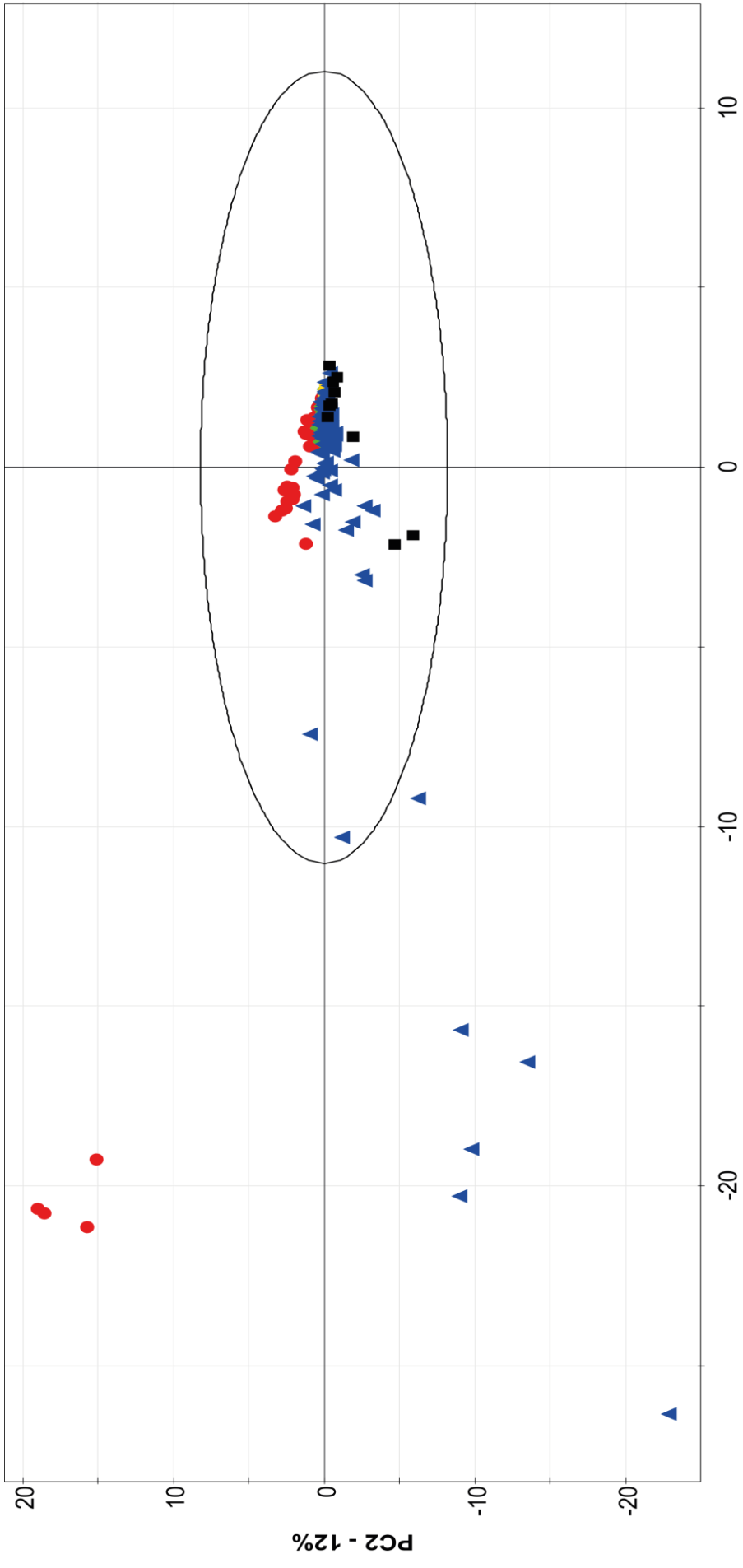


Figure 4-5. PCA scores plot displaying historical data from 2008 to 2012 coloured according to water source. 33.7% of data variance is shown. Water samples are represented as follows: tap – blue trianlge; filtered – green diamond; tank – black square; bottled – red circle & reverse osmosis – gold square.

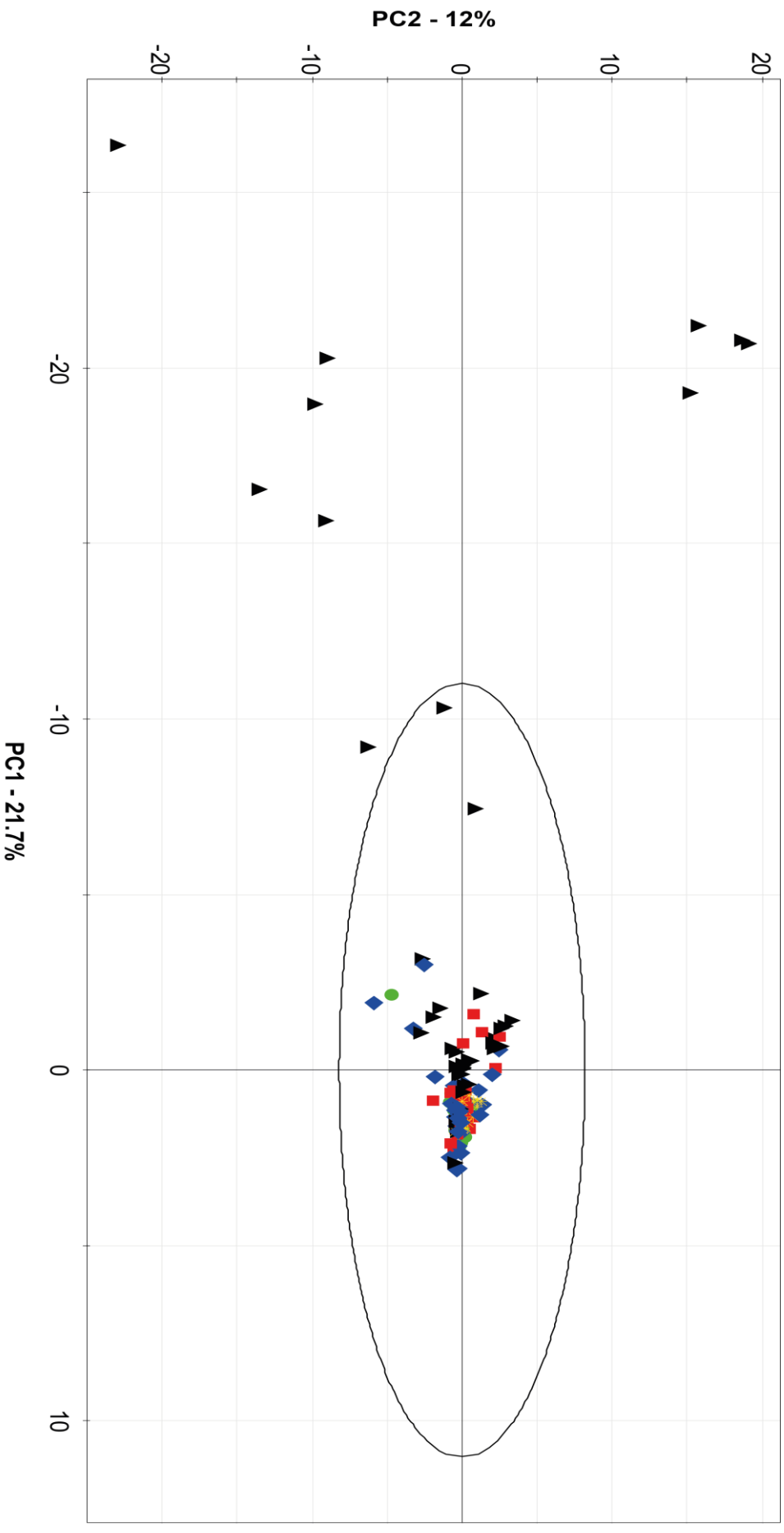


Figure 4-6. PCA scores plot displaying historical data from 2008 to 2012 coloured according to year. 33.7% of data variance is shown. The individual yearly batches are represented as follows: 2008 – green circle; 2009 – blue diamond; 2010 – gold star; 2011 - black triangle & 2012 - red square.

The lack of distinct clustering according to either potable water sources or yearly batches was unexpected and initiated investigations into each yearly batch of data.

Upon separately investigating yearly batches, batch clustering, rather than clustering according to potable water sources, was observed within each year of data when analysed individually.

The most obvious example of batch clustering is demonstrated by the data collected in 2012. Figure 4-7, the PCA scores plot, is coloured according to the four different sources of potable water collected throughout 2012. A total of 36.3% of data variance is explained, which is considered low and may attribute to the poor clustering seen here in Figure 4-7. Clearly defined clusters supporting this colour-coding of tap, tank, filtered and bottled water are not observed.

In contrast, if the data collected in 2012 are colour coded according to batch (four batches collected in this year) as in Figure 4-8, batch clustering becomes obvious.

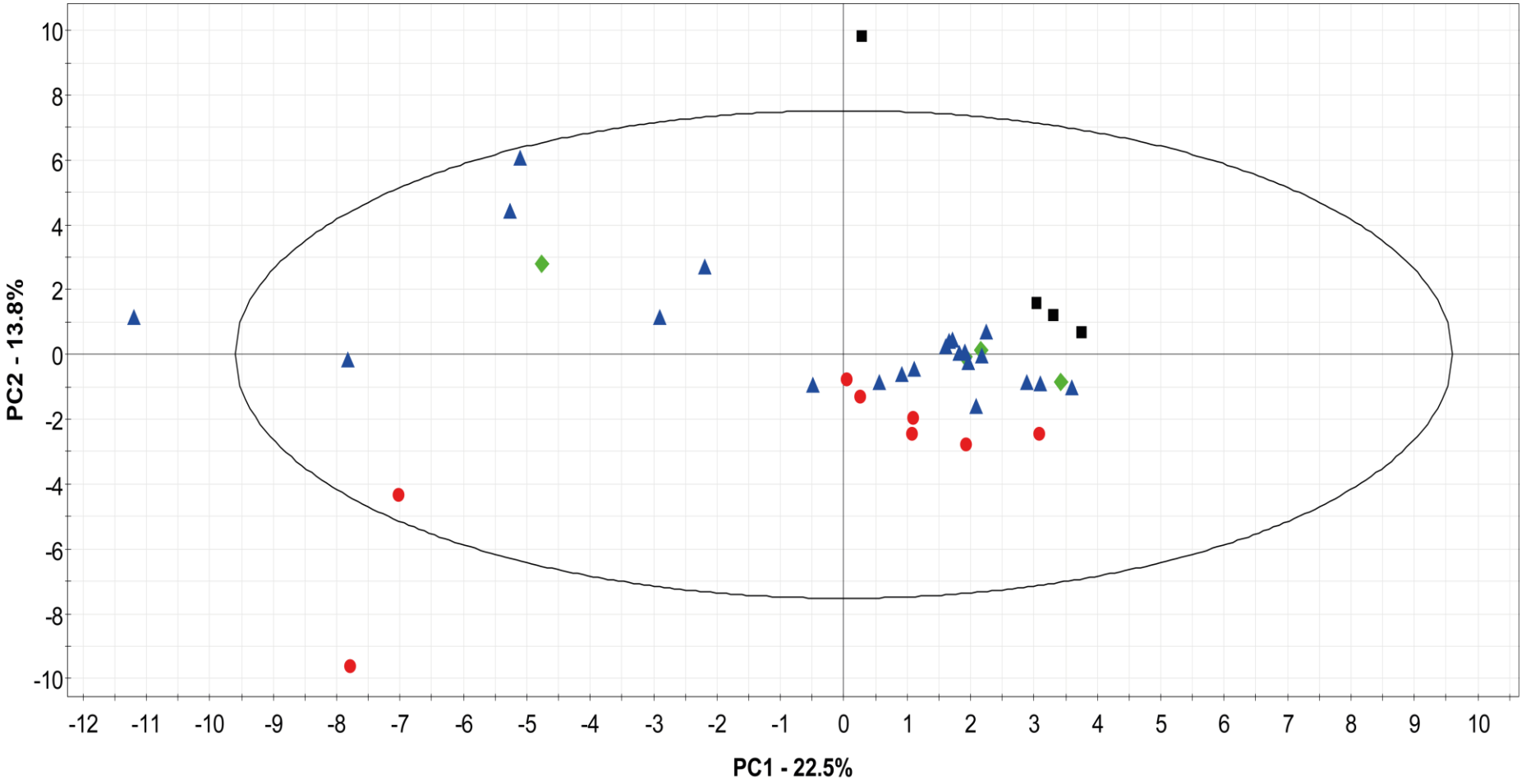


Figure 4-7. PCA scores plot displaying data collected in 2012 and coloured according to potable water sources. 36.3% of total data variance is shown. Water samples are represented as follows: tap – blue triangle; filtered – green diamond; tank – black square & bottled – red circle.

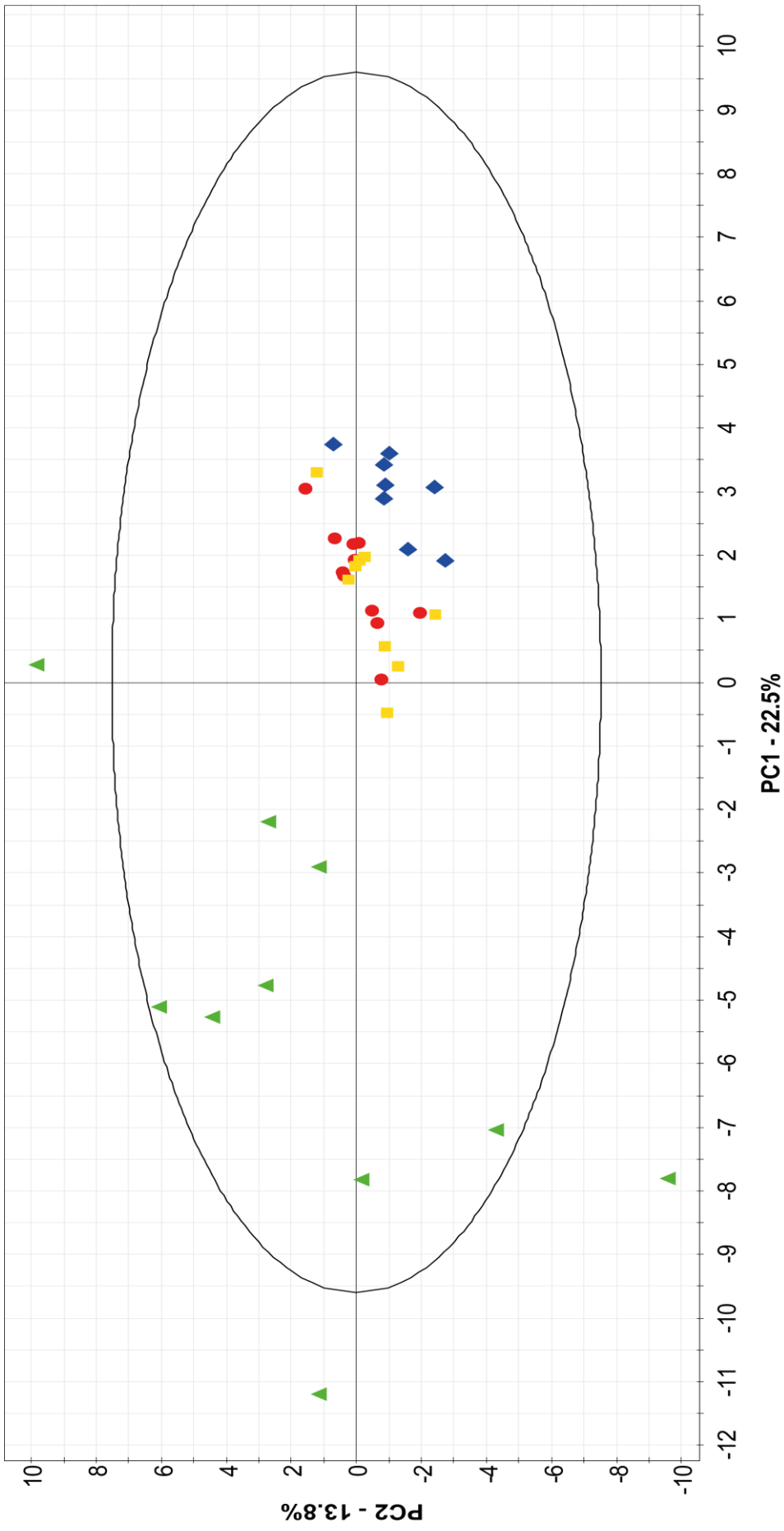


Figure 4-8. PCA scores plot displaying data collected in 2012 and coloured according to batches analysed. 36.3% of total data variance is shown. Batches are represented as follows: April 17 – green triangle; April 27 – gold square; May 1 – red circle & May 15 – blue diamond.

In Figure 4-8, two of the four batches analysed are clearly distinct, while batches analysed on April 27 (gold) and May 1 (red) overlap. Similar batch clustering was observed when all years of this longitudinal study were analysed individually.

Clustering according to individual batches analysed is more defined than clustering according to potable water sources, as demonstrated by Figure 4-7 and Figure 4-8.

The repeated clustering of batches within each year by PCA, in favour of potable water sources, was believed to be the result of run bias and instrument drift. Consequently, the hypothesis that the data will cluster according to potable water source must be revisited. Based on the results of PCA analysis so far, the modified hypothesis is that the pooled yearly data obscures trends in the data because of run bias from batch to batch. The implication is therefore that the similarities or trends of water source types that were initially expected are within the run bias of the analytical methodology used.

4.1.4.1 Run Bias and Instrument Drift

The inference made based on the results demonstrated by Figure 4-5 through to Figure 4-8 is that the method used to anaylse the historical data shows a large inherent run bias at the analyst level (repeatability) that, when pooled, gives a very large variability at the intra-laboratory level (reproducibility) (Hibbert, 2007). The method design for the sample collection and analysis of the historical data meant that the four to six batches of samples collected were different from year to year. Collecting data from different areas of Brisbane each year can equate to missing values when historical data is considered as a whole. This essentially means that each batch in each year was tested and analysed as an individual run. Therefore, no strict repeatability procedures, such as ensuring the same sample collection areas and testing for the exact same elements and isotopes, were enforced. The manner in which run bias contributes to the variability of the data when it is pooled at the intra-laboratory level is depicted in Figure 4-9 from Hibbert (2007).

Pooling and analysing all historical yearly data increased data variability. It was therefore assumed that if batch by batch analysis was performed, any analyst (batch) repeatability inconsistencies would not be affected by this intra-laboratory reproducibility problem (of increased data variability). Consequently, it was assumed that this bias could be (temporarily) overlooked, and the analysis of individual batches would be more informative of trends in the data.

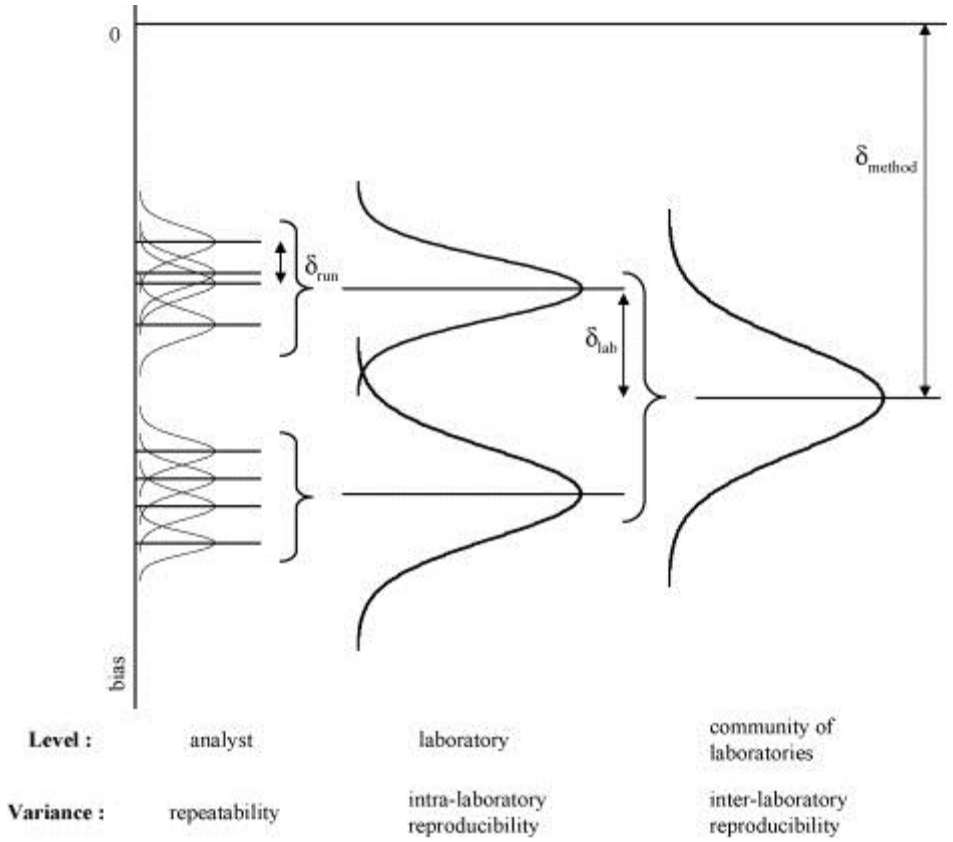


Figure 4-9. Systematic errors for a method with a large inherent run bias showing the relationship between analyst, intra-laboratory and inter-laboratory bias as defined by Thompson (2000) (Hibbert, 2007). Reprinted from Journal of Chromatography A, 1158 (1-2), D. Brynn Hibbert, *Systematic errors in analytical measurement results,* pp. 25-32, Copyright (2007), with permission from Elsevier.

In addition to any repeatability inconsistencies, the observed run bias is mainly a consequence of instrument drift. Instrument drift is a known manifestation of matrix effects (Agatemor & Beauchemin, 2011). It is the result of changes to the characteristics of the interface cones, especially small changes to the profile of the sample cone orifice, which can occur after a prolonged period of analysing samples with a high dissolved solid content (Agilent Technologies Inc., 2005a). Previous research found that a dynamic reaction cell (DRC) ICP-MS signal may drift as much as 20% in a 17 hour run, and, if left uncorrected, would result in serious loss of instrument calibration and become the biggest source of uncertainty in the employed method (Verdon et al., 2009).

The use of internal standards is a commonly employed technique for correcting long-term drift. An ideal internal standard should be a mono-isotopic species and a non-analyte isotope that does not interfere with target analytes. Isotopes commonly used are ^{9}Be, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In and ^{209}Bi (UCT Dept of Geological Sciences, 2000). Typically one to three internal standards are added to all samples and standards in the same or known concentrations. Upon addition of an internal standard to the ICP-DRC-MS method, there

was no noticeable signal drift as manifested by reproducible internal standard concentrations for the duration of the run (17 h) (Verdon et al., 2009). A second test, in which internal standard concentrations were not reproducible, displayed signal drift. Such research shows that drift can adequately be corrected through the use of internal standards.

The data collected by students from 2008 to 2012 using ICP-MS analysis used an external calibration method. The intention of the student practical was to educate students on ICP-MS and the advantage of using chemometrics. Consequently, run bias and instrument drift was not recognised until yearly data were analysed. It was resolved that an internal standard would be added to samples collected specifically for this research in 2013. The addition of an internal standard provides compensation for instrument drift and therefore, a more precise quantitative method.

In order to overcome the effects of run bias and instrument drift observed in the analysis of the historical data, individual batches were re-examined and analysed as they were by students in the past. This revealed that individual batches in each year form clusters according to expectations, where yearly batches did not.

4.1.5 Batch by Batch Chemometric Analysis of Historical Data

Despite being unable to gain significant knowledge from the yearly batches of water samples when analysed using Principal Component Analysis (PCA), a large amount of information was extracted using this technique by investigating the batches collected each year individually. In years 2008 to 2011, six batches of samples were collected, and four batches were collected in 2012. Consequently, further investigation revealed that analysis of individual batches for each year demonstrated clustering according to the original hypothesis, which stated that samples would cluster according to potable water sources.

The clustering in individual batches is best demonstrated by Batch #6 from 2008 (or Batch 08D04K00).

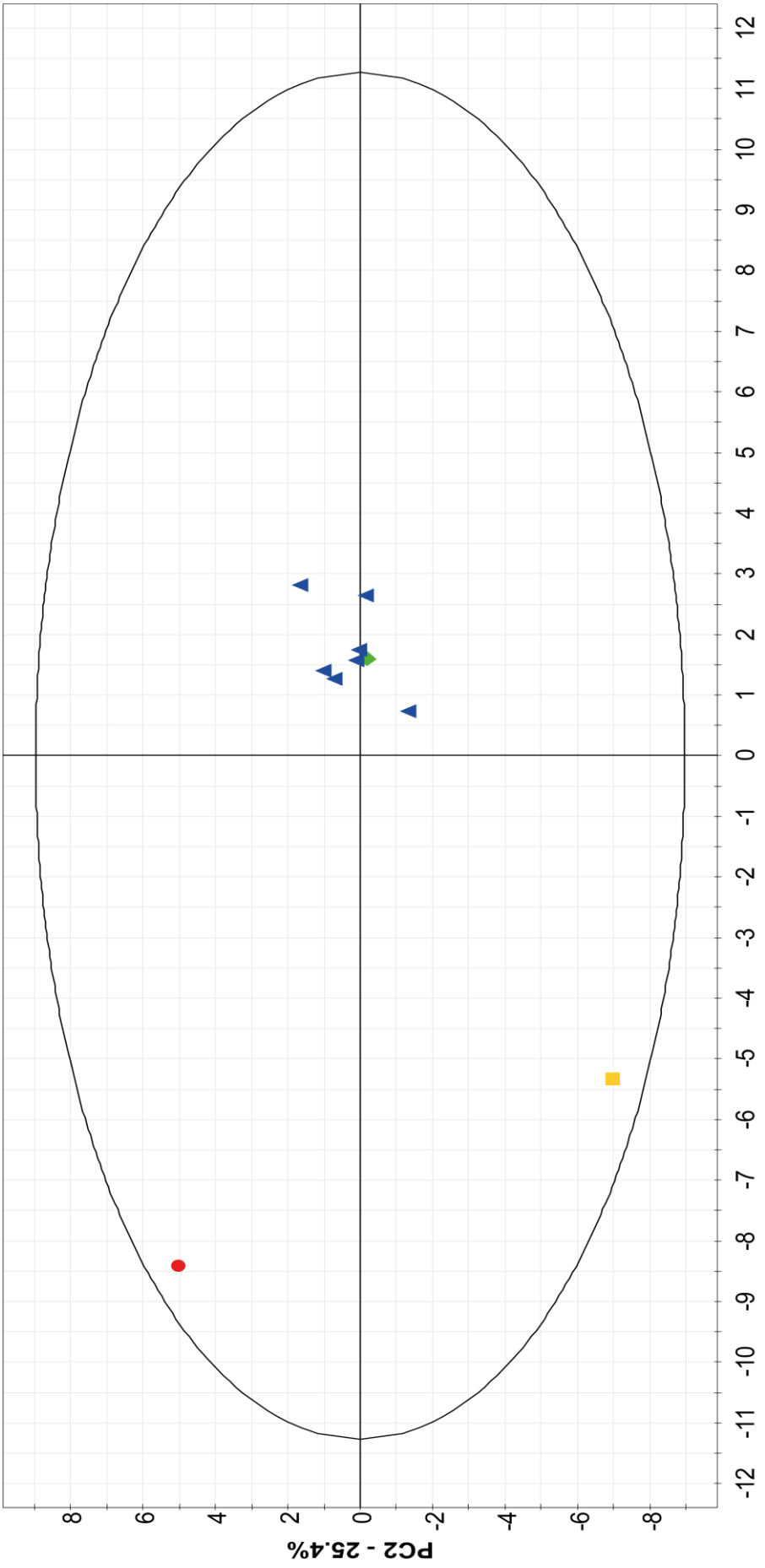


Figure 4-10. PCA scores plot displaying the separation and clustering of bottled (red circle), tap (blue triangle), filtered (green diamond), and reverse osmosis (gold square) water sources. 65.6% of the total variance is shown.

Figure 4-10 displays 65.6% of the variance in the data and shows the distinct separation of the bottled water sample, the reverse osmosis water sample, and the clustered filtered and tap water samples. Two samples, one tap and one filtered water sample, T47 (blue triangle) and F1 (green diamond) respectively, are almost inseparable on this plot. The explanation for this is that the tap water sample (T47) originated from the north-western Brisbane suburb of Bunya, and the filtered water sample was collected from the same household. Their distinction as separate water samples is clearly defined, yet the scores plot appropriately displays the obvious relationship between them.

Hierarchical Cluster Analysis (HCA) was also employed to complement the results achieved using PCA. HCA was performed using the Squared Euclidean Distance metric and the Average Linkage algorithm across all years and batches. Euclidean distance is a standard mathematical measure of distance, and is the square root of the sum of squared differences. Therefore, the Squared Euclidean Distance method uses the square of the Euclidean method. This method was chosen as distances that appear large under the Euclidean method appear even larger using the squared method, therefore contributing to complete and clear separation of clusters. Also, the Squared Euclidean Distance method was recommended by Minitab 16 Statistical Software to complement the use of the Average Linkage method chosen, whereby a more central measure of location is used through the determination of the mean distance between one observation in one cluster and an observation in another cluster. Finally, the cluster analysis displayed all results in the form of a dendrogram, or tree diagram, allowing clear assessment of clusters.

The same data for Batch #6 from 2008 (or Batch 08D04K00) used to create the PCA scores plot in Figure 4-10 was used to create the dendrogram in Figure 4-11.

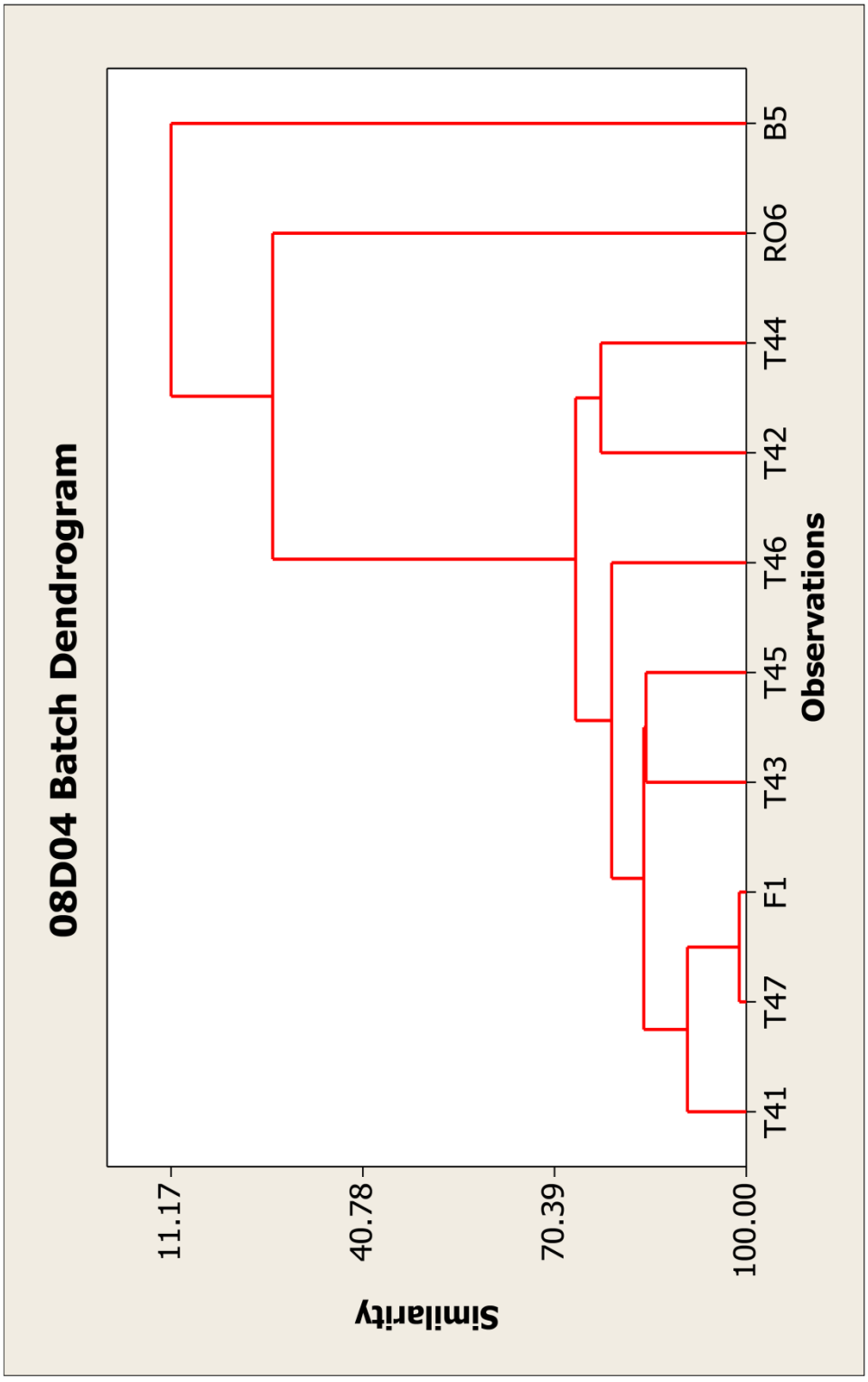


Figure 4-11. HCA Dendrogram displaying the relationship between bottled (B), tap (T), filtered (F) and reverse osmosis (RO) water samples. The similarity of samples increases down the branches of the dendrogram.

The same conclusions can be drawn from Figure 4-11. The bottled water and reverse osmosis water samples form their own branches or clusters, while the remaining tap and filtered water samples are contained in a central cluster. The most similar pairing within the tap water cluster is the relationship between the tap (T47) and filtered (F1) water samples, where both samples were collected from the same household in Bunya. These HCA results corroborate those achieved with PCA.

Figure 4-12 shows the first batch of samples tested in 2010 (Batch #1 or Batch 10D27P00), and is another clear example of clustering between potable water sources. Two brands of bottled water, "From the Springs of Rome" and "Perrier" (B1 and B2), were analysed as well as three tap water samples, two from within Brisbane city (T1 and T2) and one sample from Ascot (T3), a suburb 7 km from the Brisbane CBD.

Figure 4-12 shows a large portion, 78.6%, of the data variance for the first batch of 2010. Discriminate clustering is observed, where the tap water samples are distinct from the bottled water samples analysed. Additionally, the distance between bottled water samples is indicative of the difference between bottled water brands.

Similarly, Figure 4-13, the HCA dendrogram, shows that the tap water samples are the most similar, followed by the bottled water samples. The similarity between samples T1 and T2 that were both collected from within Brisbane city is also clearly observed. Additionally, the tap and bottled water clusters are linked, identifying the relationship between these two potable water sources.

Once again, the results of Hierarchical Cluster Analysis verify the results achieved with PCA. Therefore, the use of these complementary chemometric techniques was continued throughout this research.

These example PCA scores plots and HCA dendrograms, displayed from Figure 4-10 to Figure 4-13, show batches that are distinctly representative of all batch by batch analyses, and the same general trends observed in these examples were followed in all analyses performed. All batch chemometrics are presented in Figure 6-5 to Figure 6-30 in Appendix C-1.

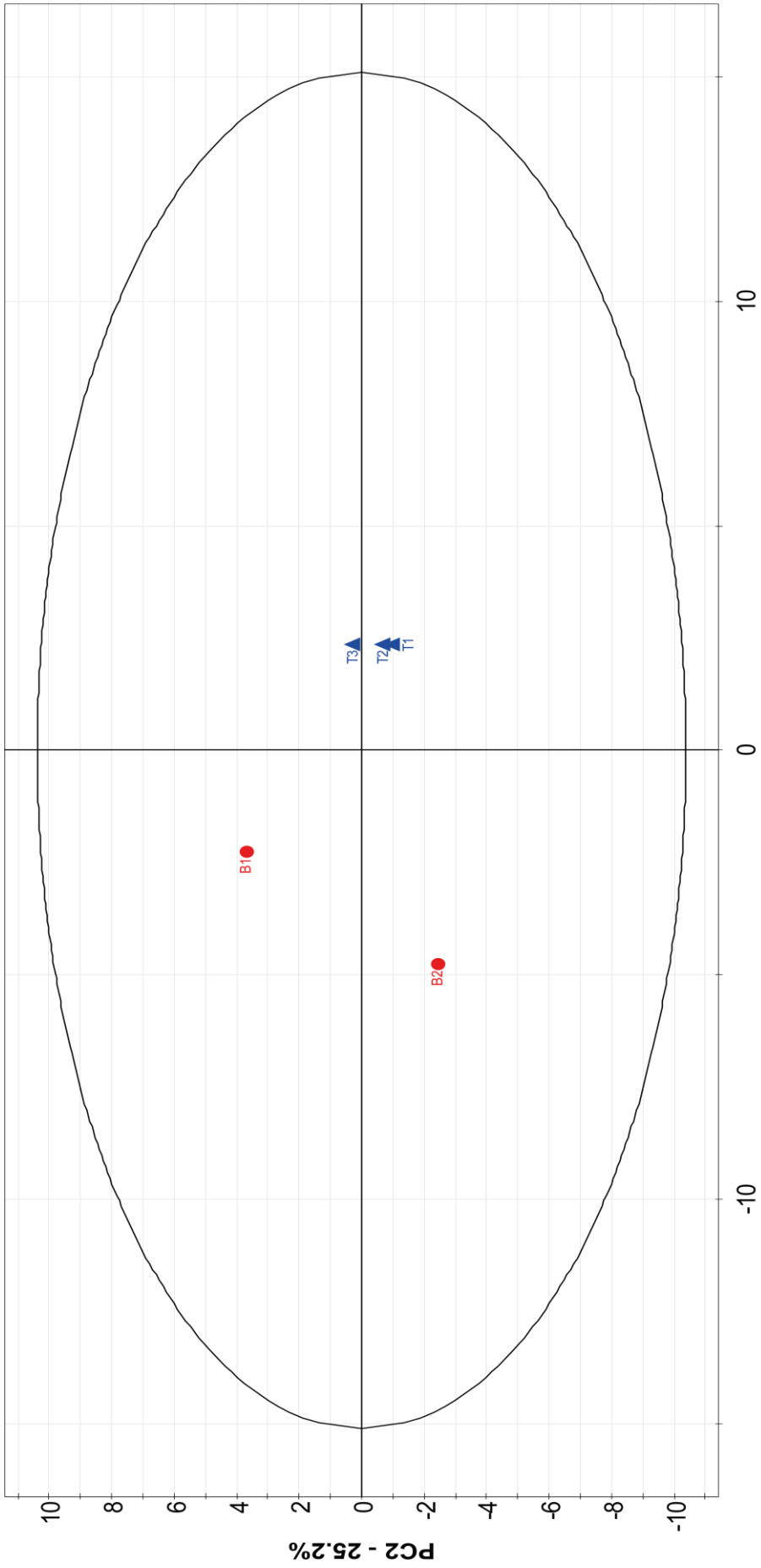


Figure 4-12. PCA scores plot showing the distinction between bottled (B – red circle) and tap (T – blue triangle) water samples in Batch 10D27P00. 78.6% of data variance is displayed.

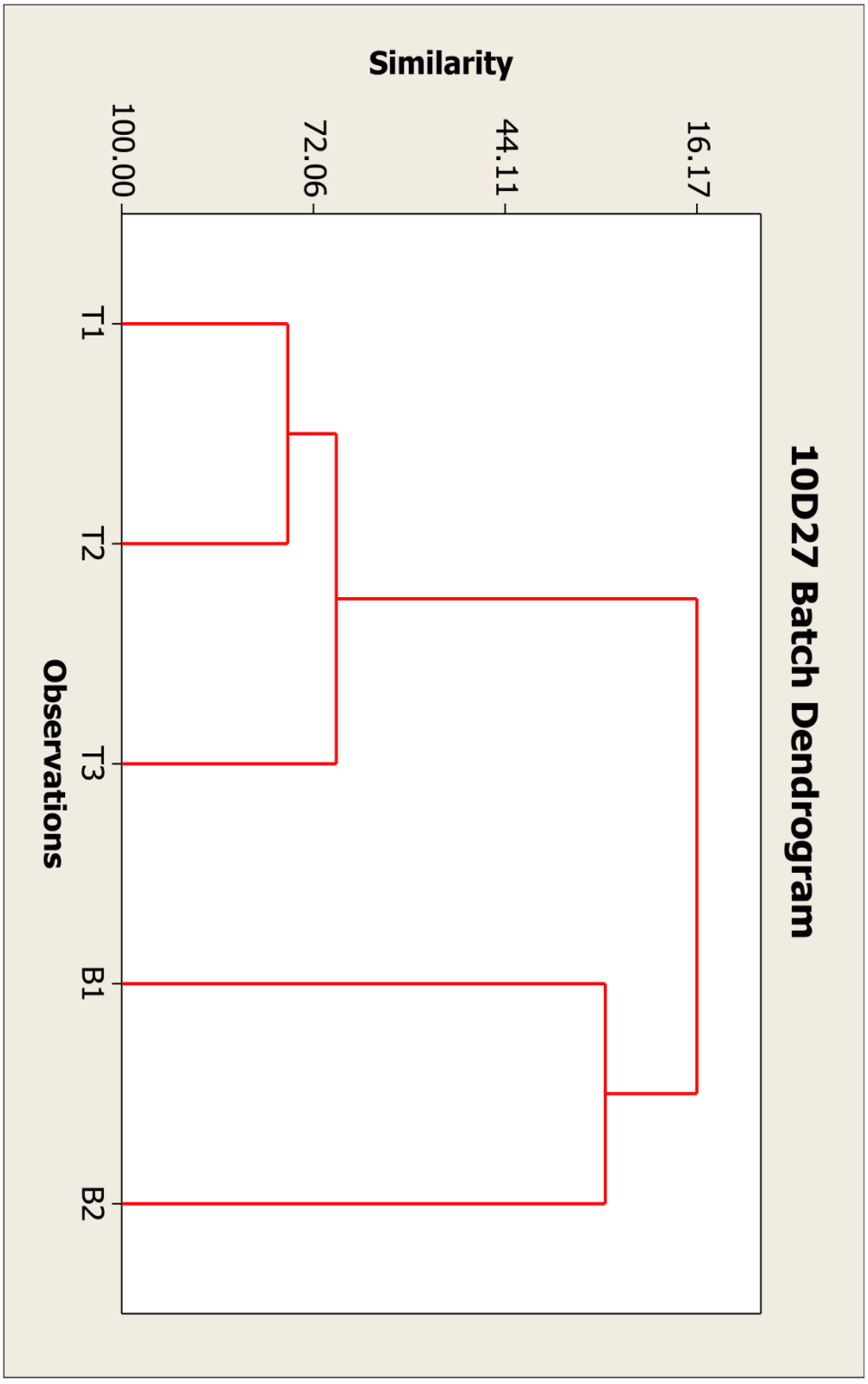


Figure 4-13. HCA Dendrogram displaying the distinction between bottled (B) and tap (T) water samples in Batch 10D27P00.

Another product of PCA analysis is a loadings plot. Rather than displaying objects, in this case water samples, a loadings plot displays the variables of the data matrix, which in this research are the trace elements and heavy metals that were analysed. PCA scores and loadings plots can be analysed alongside each other to assess the influence the trace elements and heavy metals have on different water source. Figure 4-14 is the PCA loadings plot for Batch #6 from 2008 (08D04K00), corresponding to Figure 4-10.

By examining Figure 4-10 together with Figure 4-14, it can be stated that elements such as zinc, copper, lead and manganese are the elements have the greatest association with the tap and filtered water cluster. This association is very reasonable due to the majority of household pipes being made from copper, while zinc and lead are commonly found in tap fixtures and soldering materials used, and manganese is a naturally occurring metal found in groundwater. An excess of this element is often responsible for making potable water appear brown.

Calcium, cobalt, iron, uranium and beryllium are associated with the bottled water sample in this batch, and finally, silver, thorium and thallium are linked to the reverse osmosis water sample. Several elements, including nickel and molybdenum are at a 90 degree angle in relation to the elements associated with the tap water cluster, allowing the conclusion that these groups of elements are independent from each other. Finally, magnesium, potassium, sodium, vanadium and even arsenic are the elements furthest away from the origin of this loadings plot (on the far right), therefore suggesting that they also significantly contribute to the variance of the tap and filtered water cluster, which was similarly observed on the right hand side of the scores plot in Figure 4-10.

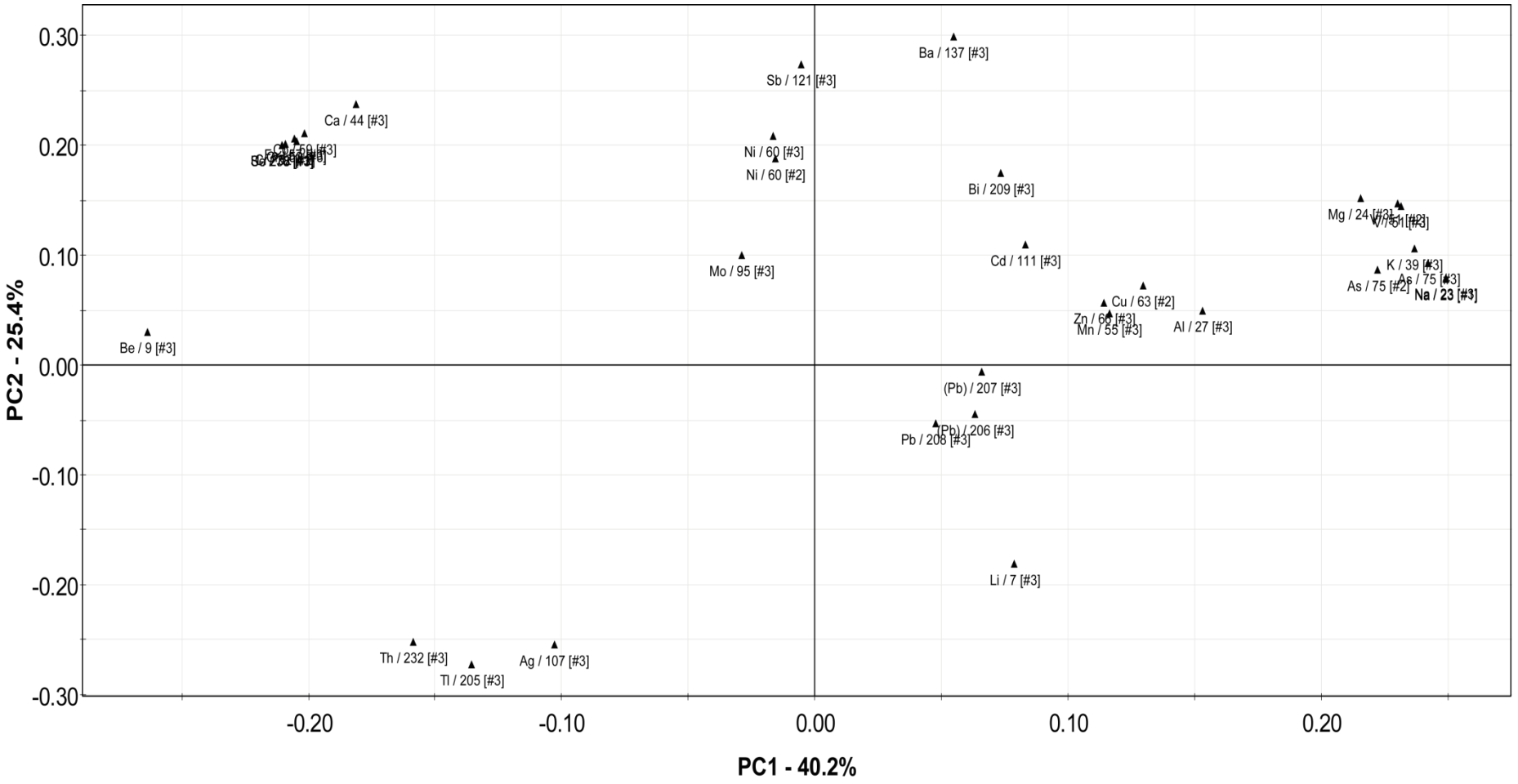


Figure 4-14. PCA loadings plot for batch 08D04K00, corresponding to Figure 4-10 and similarly displaying 65.6% of the data variance.

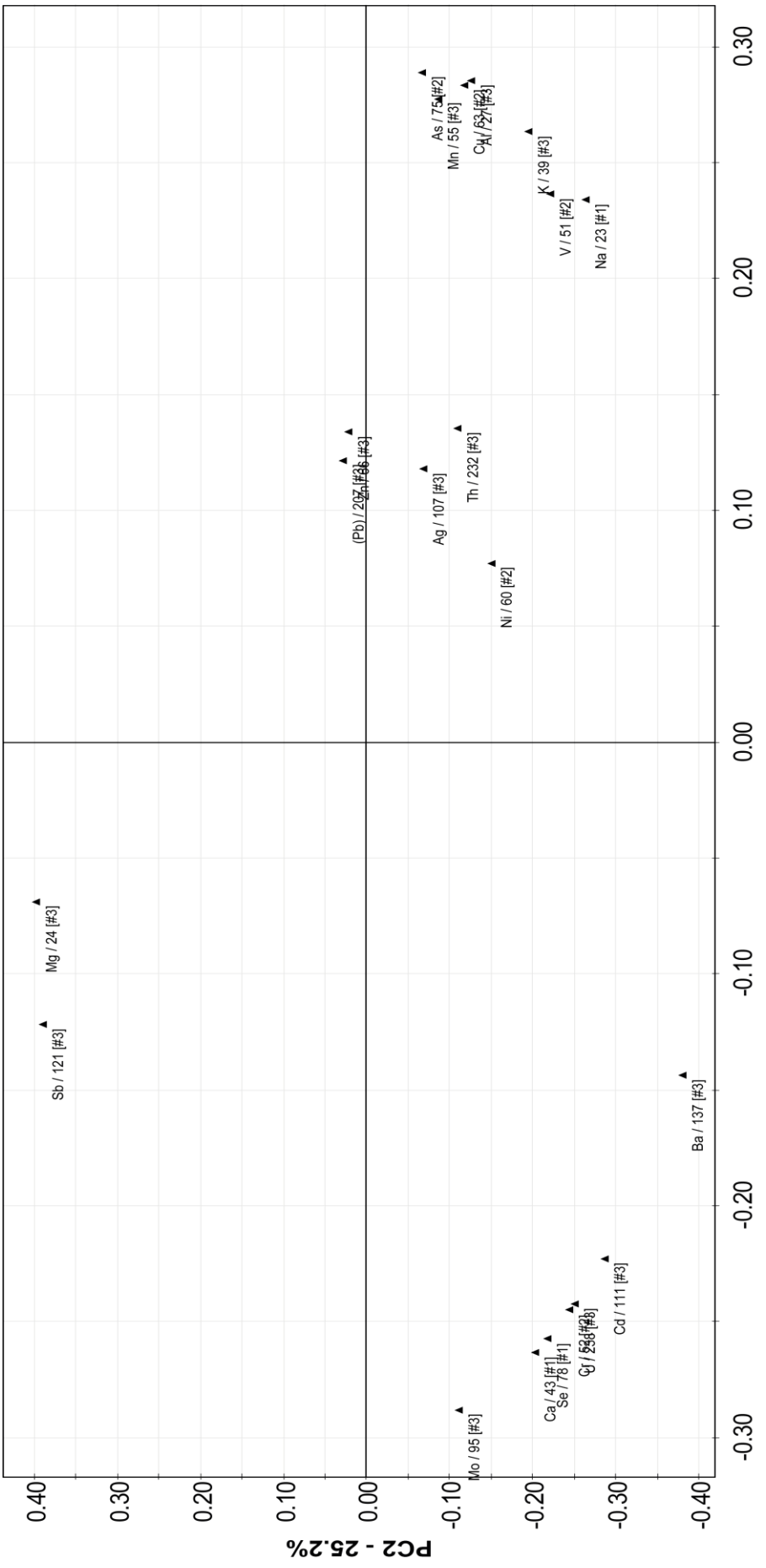


Figure 4-15. PCA loadings plot for batch 10D27P00, corresponding to Figure 4-12, displaying 78.6% of data variance.

By similarly examining the relationship between the PCA scores and loadings plots of Figure 4-12 and Figure 4-15, the trace elements and heavy metals influencing the clustering of tap and bottled water samples in batch 10D27P00 can be identified.

Very similar associations can be made for Figure 4-15, the loadings plot corresponding to Figure 4-12. Based on their positioning in the positive and negative quadrants on both sides of the loadings plot, it can be seen that copper, manganese, potassium, sodium, lead, zinc and nickel are all associated with tap water. Additionally, calcium, molybdenum, uranium, antimony and magnesium are linked to the bottled water samples.

The confirmation that different types of water samples can be separated by multivariate statistical techniques following analysis via ICP-MS is significant because it fulfils one of the main objectives of this research, by determining that water from different sources can indeed be distinguished and fingerprinted.

Additionally, these results indicate that concentrations of metal ions alone can accomplish characterisation of water sources and may therefore have the ability to be predictors for water quality. Future analysis to be presented in this research will use the Partial Least Squares (PLS) multivariate technique to establish if metal ions can be predictors for water quality. Next, the results of raw data and chemometric analyses on samples collected for this research in 2013 will be presented and discussed.

4.2 2013 Sample Collection and Analysis

On the basis of knowledge gained from assessing ICP-MS data and the subsequent chemometric analyses on the data collected by student groups from 2008 to 2012, samples collected for analysis in 2013 included a wider, more encompassing sample area. Additionally, an internal standard was employed when using ICP-MS, in line with the original US EPA Method 200.8 that stated that internal standardisation must be used in all analyses to correct for instrument drift and physical interference (US EPA, 1994). The inclusion of an internal standard was a step taken to eliminate run bias and instrument drift, and was afforded due to the availability of more time (than student groups) and the desire for this research to improve on the accuracy and precision of previous work.

Similarly, the additional use of the specific PA Tuning Solution (not used in previous years) as suggested by the Agilent ChemStation Operators Manual contributed to superior results due to the successful calibration between the pulse and analog counting signals in the instrument set up.

Sample collection and preservation procedures were carried out as described in section 3.5 of Chapter Three. All samples (excluding the unopened bottled water samples purchased) were collected in PET containers that had been soaked in 10% nitric acid for a minimum of 24 hours, and were all transported in an Esky© back to the laboratory where each sample was filtered into a fresh sample container through a 0.45 µm Merck Millipore filter and acidified with 70% nitric acid to pH≤2. Finally, 40 µL of internal standard was added and the samples were refrigerated for preservation.

4.2.1 Sample Collection Information

In 2013, sample collection was undertaken on a June long weekend, beginning on Friday June 7 with raw and treated water sample collection, through to Monday June 10 with potable sample collection. Mains water sample collection took place on Tuesday June 11, and bottled water was purchased and prepared on Thursday 13 June. Additionally, employees at water transportation company H_2Flow were given sample containers with which to collect potable (and mains) water samples in the same week, Wednesday June 5 to Monday June 10. Complete sample information is contained in Table 6-2 to Table 6-6 in Appendix C-2. The following maps, Figure 4-16 to Figure 4-20, are marked with the areas or specific homes visited according to these tables. Additionally, a variety of bottled water brands were purchased from Coles in Brisbane city and tested for a complete analysis of potable water sources available in South East Queensland.

As demonstrated in Table 6-2 and Table 6-3 in Appendix C-2, potable water, as tap, tank and filtered water samples were collected from 110 locations in the greater Brisbane area, extending from Kallangur in the north, the Gold Coast in the south, Victoria Point in the east, and Mt Crosby out west. To better visualise the number and spread of the samples collected, the locations visited were plotted on a map of South East Queensland, as seen in Figure 4-16.

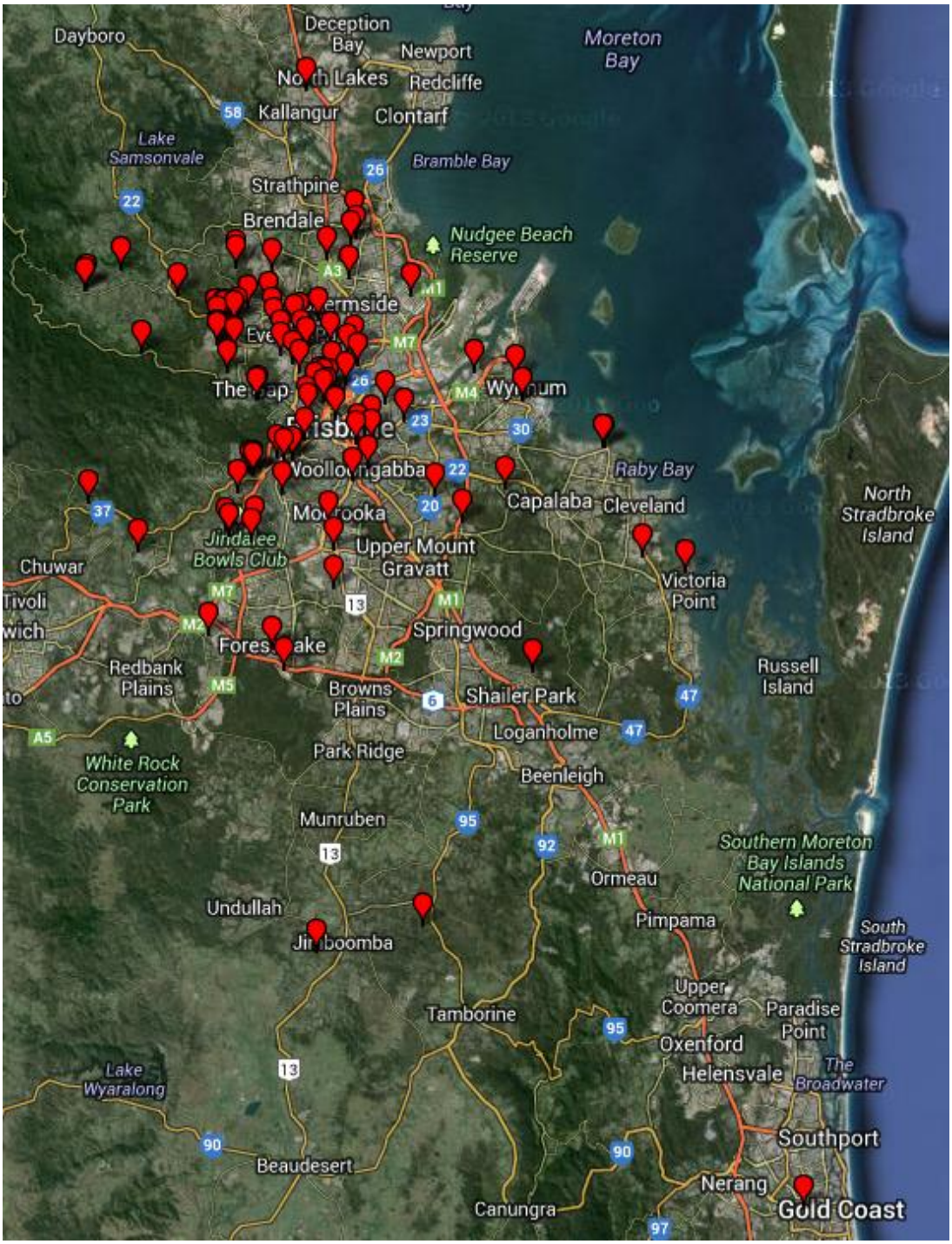


Figure 4-16. Map of South East Queensland overlaid with all sample locations visited from June 5 to June 10, 2013. This map corresponds to the addresses and information listed in Table 6-2 and Table 6-3 in Appendix C-2.

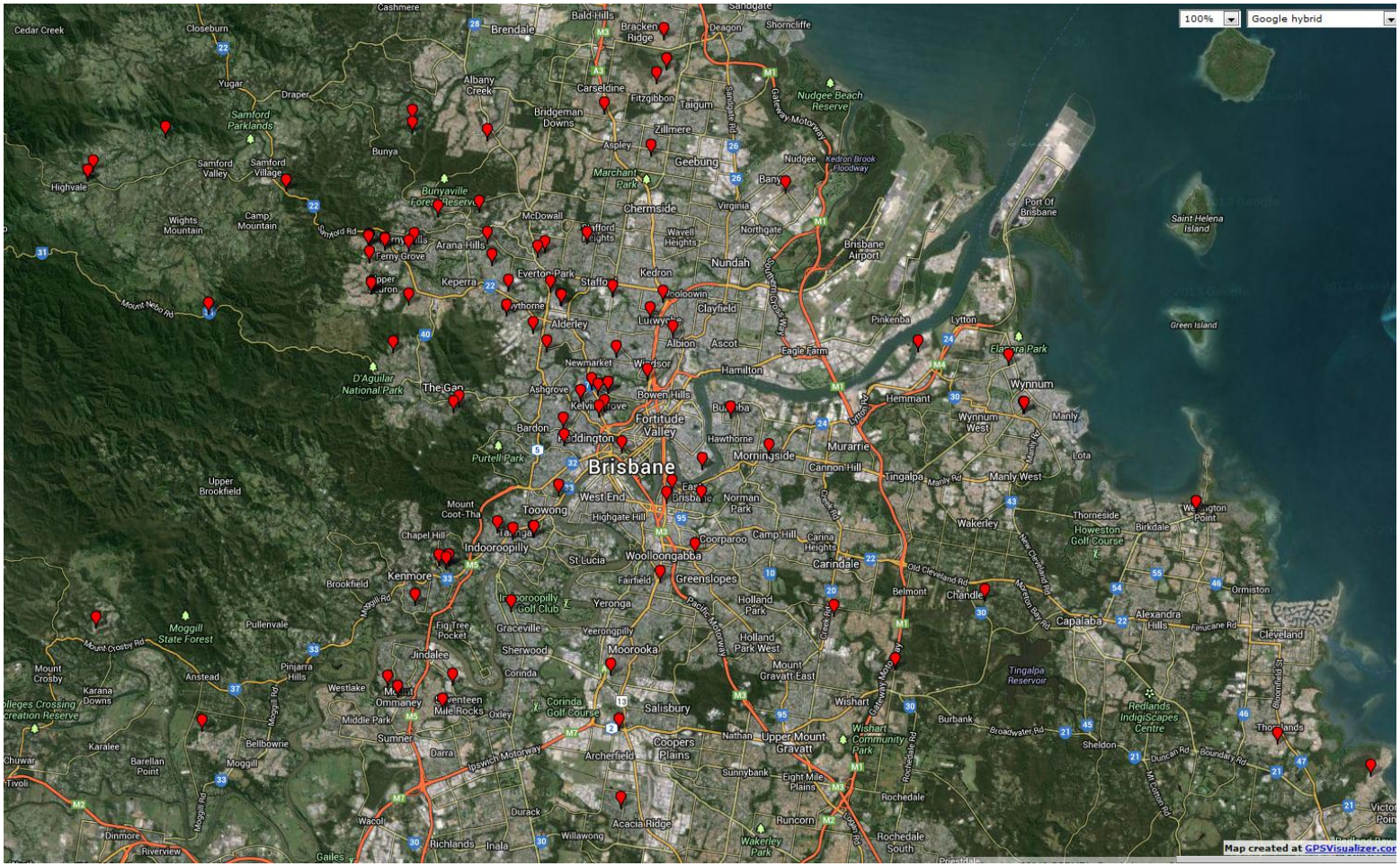


Figure 4-17. A magnification of Figure 4-16, this map better displays the spread of sample sites visited in close proximity to Brisbane city itself.

In addition to collecting potable water samples from homes in the greater Brisbane area, raw water samples were collected from the areas displayed in Figure 4-18. Two treated water samples were also collected from Mt Crosby WTP (marked on Figure 4-18).

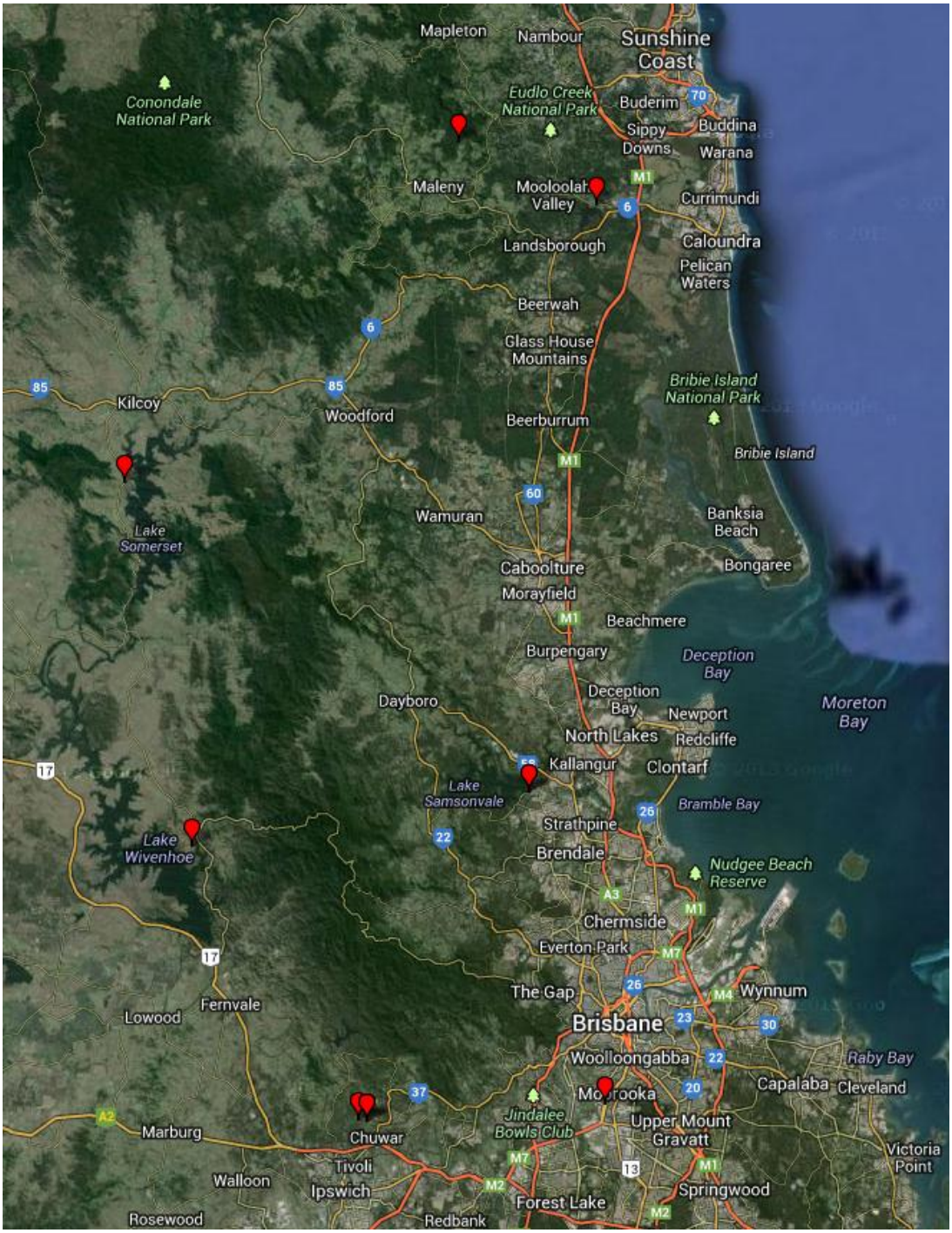


Figure 4-18. Map corresponding to Table 6-4 in Appendix C-2, marked with the locations where raw water samples were collected on June 7, 2013. Mt Crosby West Bank WTP, where the treated water samples were collected, is also marked.

Lake Somerset was one of the locations from which raw water was collected for this research. A description of each raw water source visited was recorded for complete sample information. Shown in Figure 4-19, the public access area of Lake Somerset that was visited is known as “The Spit”, where a boat ramp and picnic and recreational areas are located. The presence of wildlife was apparent, and the beautiful clear water had an overall brown appearance due to the dirt surface of Lake Somerset.

Figure 4-19. "The Spit" on Lake Somerset, where recreational activities such as picnicking, boating and fishing are popular.

Finally, Figure 4-20 shows where mains water samples were collected with the assistance of water transportation company H_2Flow. These samples were collected from various suburbs that had not been visited during potable water sample collection, ensuring the widest possible spread of samples.

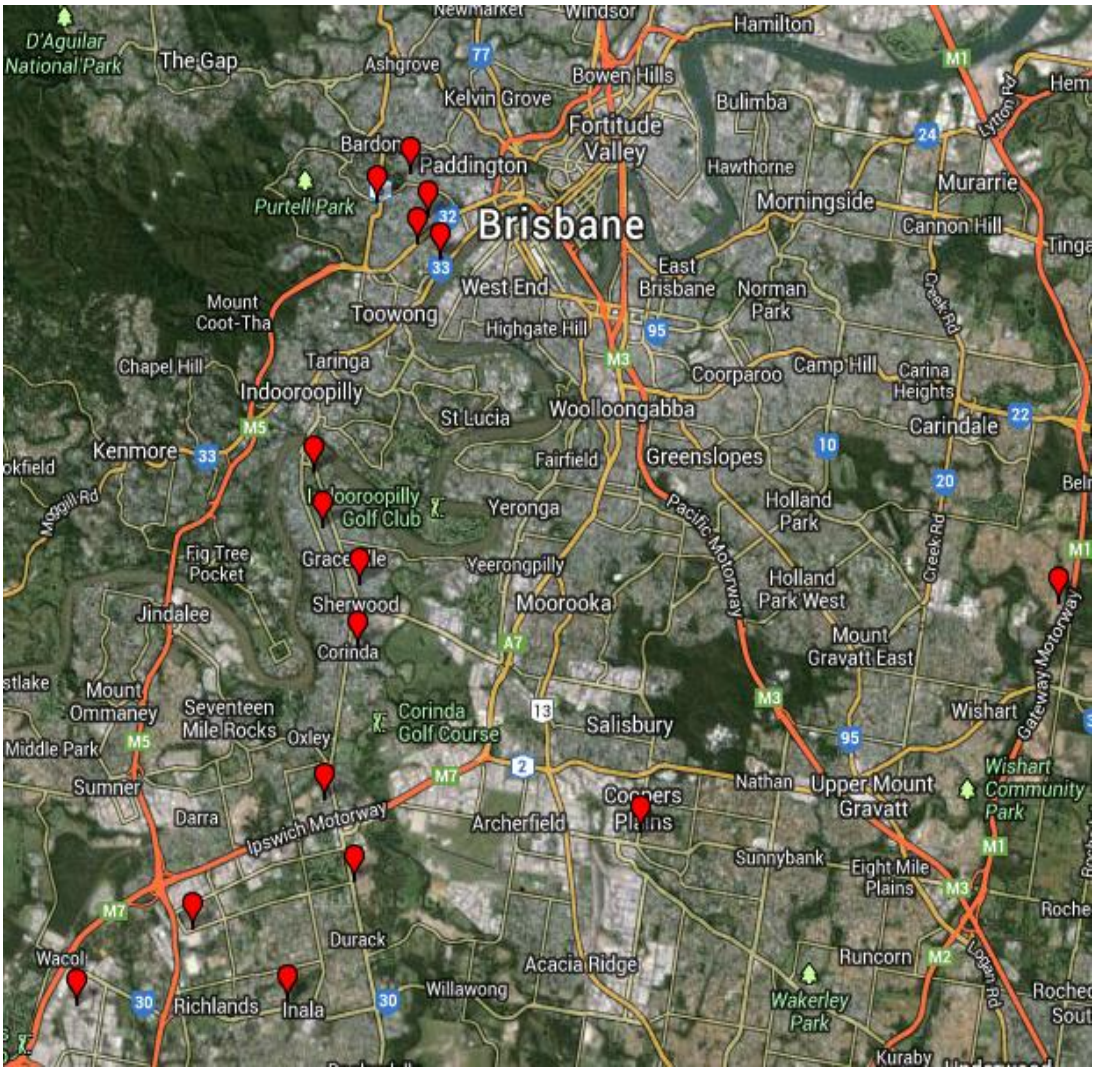


Figure 4-20. Map corresponding to Table 6-5 in Appendix C-2, showing the suburbs from which mains water was collected via a stand pipe on June 11, 2013.

Mains water collection was facilitated by a stand pipe. First, the main was uncovered and cleaned out, the stand pipe was inserted and then the tap was turned to initiate the flow of water. Often, this inital flow was allowed to continue for up to a minute before sampling occurred, as dirt persisting in the main contaminated the mains water that flowed through the stand pipe. Once water flowed clear, the sample was taken. This process is depicted in Figure 4-21.

Figure 4-21. Mains water collection was facilitated by a stand pipe and the support of water transportation company H_2Flow.

4.2.2 ICP-MS Analysis

Prior to performing sample analysis via ICP-MS, five calibration standards including all elements of interest were made to varying concentrations as described in section 3.5.3 of Chapter Three.

4.2.2.1 Standard Corrections

In order to perform analysis via ICP-MS, the trace element and heavy metal concentrations of the samples collected must be compared to five calibration standards: a blank and four known concentrations. To achieve varying concentrations, the different volumes of the Agilent Environmental Calibration Standard and Mercury Single Element Standard required were calculated and delivered to each flask, and were weighed for accuracy. Whilst intended concentrations of standards were input when samples were analysed by ICP-MS, the concentrations were later corrected to reflect the actual concentration of each standard based on the masses recorded.

Table 4-5. Summary of the dilutions and concentrations of each (external) calibration solution (in µg/L), the volumes of each Agilent Standard required, and the recorded mass delivered for all standard solutions.

Dilution	**Blank**	1-to-20,000 **(Std 1)**	1-to-10,000 **(Std 2)**	1-to-1000 **(Std 3)**	1-to-100 **(Std 4)**
For microelements: **10 mg/L** of Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn, Th and U; Hg.	Blank	0.5 µg/L	1 µg/L	10 µg/L	100 µg/L
For macroelements: **1000 mg/L** of Fe, K, Ca, Na and Mg	Blank	50 µg/L	100 µg/L	1000 µg/L	10,000 µg/L
Agilent Environmental Calibration Standard (#5183-4688)	0µL	12.5 µL	25 µL	250 µL	2500 µL ≈2.5 mL
Mass (g)	(N/A)	0.0128	0.0260	0.2737	2.6191
Single Element Standard – Mercury (#8500-6941)	0µL	12.5 µL	25 µL	250 µL	2500 µL ≈2.5 mL
Mass (g)	(N/A)	0.0129	0.0257	0.2686	2.5810

Calculations were performed to determine the actual concentration of each calibration standard based on the mass of the volume delivered to each 250 mL volumetric flask. As a result, the actual concentrations of the calibration standards used in the ICP-MS analysis for this research are summarised in Table 4-6.

Table 4-6. Summary of the volumes, mass recorded, intended concentrations and mass-corrected concentrations of all calibration standards used in this ICP-MS analysis.

Dilution	Units	Blank	1-to-20,000 (Std 1)	1-to-10,000 (Std 2)	1-to-1000 (Std 3)	1-to-100 (Std 4)
Agilent Environmental Calibration Standard (#5183-4688) *10 mg/L microelements & 1000 mg/L macroelements*	**µL**	0	12.5	25	250	2500 2.5 mL
Mass (g) of #5183-4688 Standard delivered	**g**	(N/A)	0.0128	0.0260	0.2737	2.6191
Intended *Concentration – Microelements (10 mg/L):* Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn, Th and U.	**µg/L**	Blank	0.5	1	10	100
Corrected Concentration - Microelements	**µg/L**	(N/A)	0.512	1.040	10.95	104.8
Intended *Concentration – Macroelements (1000 mg/L):* Fe, K, Ca, Na and Mg.	**µg/L**	Blank	50	100	1000	10,000
Corrected Concentration - Macroelements	**µg/L**	(N/A)	51.2	104	1095	1.048×10^4
Single Element Standard – Mercury (#8500-6941)	**µL**	0	12.5	25	250	2500 2.5 mL
Mass (g) of #8500-6941 Standard delivered	**g**	(N/A)	0.0129	0.0257	0.2686	2.5810
Intended *Concentration - Hg:*	**µg/L**	Blank	0.5	1	10	100
Corrected Concentration - Hg	**µg/L**	(N/A)	0.516	1.028	10.74	103.2

From Table 4-6 it is evident that more than the intended concentration was added to each of the calibration standards. The uncertainty associated with these calculated concentrations can easily be determined by dividing the difference between the corrected and intended concentrations by the corrected concentration, and finding the percentage. The results of these calculations are displayed in Table 4-7.

Table 4-7. The percentage uncertainty values associated with the concentrations of each of the standard solutions used to make up the Calibration Standards.

		Concentration (µg/L)	Uncertainty (±)
Standard 1 (1-to-20,000)	*Microelements*	0.512	2.34%
	Macroelements	51.2	
	Mercury	0.516	3.10%
Standard 2 (1-to-10,000)	*Microelements*	1.040	3.85%
	Macroelements	104	
	Mercury	1.028	2.72%
Standard 3 (1-to-1000)	*Microelements*	10.95	8.68%
	Macroelements	1095	
	Mercury	10.74	6.89%
Standard 4 (1-to-100)	*Microelements*	104.8	4.58%
	Macroelements	1.048×10^4	
	Mercury	103.2	3.10%

The uncertainty values calculated in relation to the intended concentrations of each standard demonstrate the uncertainty associated with the Eppendorf pipettes and pipette tips used in making up the calibration standards for this research. With the exception of Standard 3, the uncertainty associated with Standards 1, 2 and 4 is less than 5%. Because the standard concentrations were mass-corrected and the data collected via ICP-MS reprocessed according to the 'Corrected Concentration' as shown in Table 4-6, the most accurate results possible were achieved.

4.2.2.2 Internal Standard Corrections

In addition to correcting for mass for the external calibration standards, the Internal Standard volume individually added to each sample was also weighed for maximum accuracy.

As described in section 3.5.2 of Chapter Three, all samples were filtered, acidified and refrigerated for preservation on the date they were collected. Three drops of RCI Premium 70% nitric acid was administered to every sample, as was 10 µg/L (40 µL in 40 mL of sample) of Internal Standard. The mass of Internal Standard used on each day was recorded in Table 4-8 for maximum accuracy. All ICP-MS analytical runs were completed using the concentration of 10 µg/L of Internal Standard; however, this was later corrected to the average concentration of Internal Standard delivered per run. An average had to be used due to the combination of samples set up in sequence for ICP-MS analysis.

Table 4-8. The mass of Internal Standard added to each sample on the day it was collected.

Date samples were collected	Mass of 40 µL Internal Standard added per sample (g)
June 7, 2013 (Friday)	0.0408
June 8, 2013 (Saturday)	0.0413
June 9, 2013 (Sunday)	0.0411
June 10, 2013 (Monday)	0.0411
June 11, 2013 (Tuesday)	0.0411
June 13, 2013 (Thursday)	0.0411

Similarly, Internal Standard was added to the calibration standards after 40 mL of each standard was transferred to sample tubes ready for ICP-MS analysis. The same standards were used for the whole analysis, however, the 40 mL volume of standard in the sample tube was discarded and replenished for each of the three batches, and thus new Internal Standard was added to the standards, as shown in Table 4-9.

Table 4-9. The mass of Internal Standard added to each calibration standard as they were replenished for each ICP-MS run.

Sample Batches	Mass of 40 µL Internal Standard added per Standard (g)
June 17, 2013 *(kate17ja)*	0.0406
June 19, 2013 *(kate19ja)*	0.0407
June 20, 2013 *(kate3jua and kate4jua)*	0.0407

As well as correcting the concentration of each calibration standard based on the mass of stock standard solution added, the same process was performed for each addition of Internal Standard. That is, whilst the analysis was performed, the Internal Standard concentration used was 10 µg/L, but the concentrations were later corrected to reflect the actual concentration of Internal Standard based on the masses recorded. A summary of the actual Internal Standard concentrations calculated for all samples and standards are shown in Table 4-10.

Table 4-10. The recorded mass and resultant concentration of Internal Standard added to each group of samples and all batch standards.

Date samples were collected	Mass of 40 µL Internal Standard added per sample (g)	Actual Concentration of Internal Standard per sample (assumed 10 µg/L)
June 7, 2013 (Friday)	0.0408	10.2
June 8, 2013 (Saturday)	0.0413	10.3
June 9, 2013 (Sunday)	0.0411	10.3
June 10, 2013 (Monday)	0.0411	10.3
June 11, 2013 (Tuesday)	0.0411	10.3
June 13, 2013 (Thursday)	0.0411	10.3
Trip Blank	0.0407	10.2
Sample Batches	**Mass of 40 µL Internal Standard added per Standard (g)**	**Actual Concentration of Internal Standard per Standard (assumed 10 µg/L)**
June 17, 2013 *(kate17ja)*	0.0406	10.2
June 19, 2013 *(kate19ja)*	0.0407	10.2
June 20, 2013 *(kate3jua and kate4jua)*	0.0407	10.2

It is evident from Table 4-10 that more than 10 µg/L was added to each sample or standard. The uncertainty associated with these calculated concentrations can easily be determined.

The maximum difference in concentration was observed for samples collected and processed from June 8 to June 13, 2013, where it was calculated that 10.3 µg/L of Internal Standard was added instead of the intended 10 µg/L:

$$10.3 - 10 = 0.3\ \mu g/L$$

$$\rightarrow \frac{0.3}{10.3} \times 100\%$$

$$\therefore uncertainty = 3\%$$

Therefore, the maximum uncertainty associated with the Internal Standard added to any of the samples or standards is 3%. This is a small uncertainty value and is thus acceptable in this analysis.

As a consequence of setting up multiple analytical runs on the ICP-MS instrument, sample date groups were mixed within sequences, resulting in varying concentrations of Internal Standard present for each batch. However, it is not possible to enter multiple concentrations for Internal Standard in Agilent ChemStation software. Therefore, the average Internal Standard concentration of all the sample dates and standards (from Table 4-10) analysed per batch was used.

Batch *kate17ja* contained samples collected on Saturday and Sunday, therefore the Internal Standard concentration corrected for this batch was the average of these two sample date concentrations as well as the batch calibration standard concentration.

$$\frac{10.3 + 10.3 + 10.2}{3}$$
$$\therefore \ Average\ ISTD\ Concentration = \ 10.3\ \mu g/L$$

Batch *kate19ja* only contained samples collected on Monday; therefore the Internal Standard concentration corrected for this batch was the average of this sample date concentration and the batch calibration standards concentration.

$$\frac{10.3 + 10.2}{2}$$
$$\therefore \ Average\ ISTD\ Concentration = \ 10.3\ \mu g/L$$

Finally, batch *kate3jua* and *kate4jua* contained samples collected on Friday, Monday, Tuesday, Thursday and the individually treated trip blank. Therefore, the corrected Internal Standard concentration for this batch was the average of all these sample date concentrations as well as the batch calibration standards concentration.

$$\frac{10.2 + 10.3 + 10.3 + 10.3 + 10.2 + 10.2}{6}$$
$$\therefore \ Average\ ISTD\ Concentration = \ 10.3\ \mu g/L$$

The Internal Standard concentrations corrected as above and applied to each batch of data are summarised in Table 4-11.

Table 4-11. The averaged concentrations of Internal Standard added to each batch analysed via ICP-MS.

Sample Batches	Averaged Concentration of Internal Standard per batch µg/L
June 17, 2013 *(kate17ja)*	10.3
June 19, 2013 *(kate19ja)*	10.3
June 20, 2013 *(kate3jua and kate4jua)*	10.3

From Table 4-11, the averaged concentration of Internal Standard in each batch is 10.3 µg/L. The intended concentration of Internal Standard was 10 µg/L:

$$10.3 - 10 = 0.3\ \mu g/L$$
$$\rightarrow \frac{0.3}{10.3} \times 100\%$$
$$\therefore uncertainty = 3\%$$

Therefore, the uncertainty associated with the Internal Standard added to each batch analysed is 3%. This is a very small uncertainty value, and this, in addition to reprocessing the data collected via ICP-MS according to the corrected Internal Standard concentrations, ensured that the most accurate results possible were achieved.

4.2.3 ICP-MS Results

The initial results of an analysis by ICP-MS are displayed as a mass spectrum. The raw instrumental data consist of the counts per second recorded by the detector, which are later converted into concentration. In this research, all samples were reprocessed (offline) with the mass-corrected concentrations of calibration standards and internal standards. Agilent ChemStation software FileView32 then converted the data into quantitative concentrations (parts per billion) as specified in the method used for this research.

Next, the quantitative data were exported to Microsoft Excel, where they were treated by determining basic statistics such as mean, geometric mean, standard deviation and standard error, the minimum, maximum, range, median, and finally, quartile values. The geometric means for each individual trace element, heavy metal, and their tuning steps were used to replace missing values. The trace elements, heavy metals and tuning steps collected in each batch for the 2013 data were consistent, as opposed to data collected from 2008 to 2012, however, just a few variables were not recorded for some water samples as the concentrations were exceedingly high for the detector (reported with “E” in Quantitation Reports, and <###> when exported to FileView32). Similarly, any concentrations that were below the detection limit were displayed as negative values. Half of the Method Detection Limit (MDL) concentration for each variable was used to replace these negative values. The MDL was determined to be one third of the lowest positive concentration returned for each variable. Any negative concentrations in environmental analyses are considered erroneous, as logically, in the environment, something is either present or it is not. Raw data could then be compared to the 2011 ADWG, internally and against independent reports.

4.2.4 Raw Data Analysis of 2013 Data

Initial treatment for the determination of basic statistics for these data was the same as that applied to the historical data for the longitudinal study from 2008 to 2012. This means that any missing values were replaced with the geometric mean of the column, and any negative values were replaced with half the MDL concentration for that variable. Subsequently, these raw data were directly compared to the 2011 ADWG.

4.2.4.1 Comparison to 2011 Australian Drinking Water Guidelines

In comparing the raw 2013 data to the 2011 Australian Drinking Water Guidelines (ADWG) outlined in Table 4-4, the sampling codes, such as T#, F# and TK#, and collection locations of samples discussed can be referenced against Table 6-2 to Table 6-6 in Appendix C-2. A brief homeowner survey was conducted at the time the samples were collected, the results of which are presented in Table 6-3 in Appendix C-2. No adverse comments were made in regards to taste, odour or appearance of the drinking water. Therefore, it can be assumed that any exceedence of the aesthetic guidelines went unnoticed by homeowners.

In general, the pH of tap water collected from homes in the greater Brisbane area ranged from 7.3 to 7.6. Hardness was determined by totalling the concentrations of calcium and magnesium ions present in tap water samples. Therefore, the minimum hardness associated with tap water was 14 886 µg/L, and the maximum hardness was 136 525 µg/L.

It is important to note that the majority of tank water samples were collected from tanks made of galvanised steel, the most common material used in the manufacture of rain water tanks throughout Australia (Environmental Health Committee (enHealth), 2011). The exceptions to this were TK2 and TK10, samples collected from concrete tanks, and TK3, which was collected from a plastic tank. Similarly, filtered water samples were collected from several types of filters; some filters were built in to sinks and refrigerators, while others were filter jugs or stand-alone water filters.

The first conclusion that can be drawn from this analysis is that the concentrations obtained for mercury are inaccurate, as every sample tested returned concentrations well in excess of the guideline value of 1 µg/L for health considerations. This is a valid conclusion as previous literature has shown that the use of only nitric acid to preserve water samples produces erroneous results for mercury, and a mixture of both nitric acid and hydrochloric

acid is recommended for the preservation of mercury (Louie et al., 2012). Therefore, mercury was removed from consideration in all future raw data and chemometric analyses.

Similarly, two iron isotopes were analysed, iron 56 (^{56}Fe) and iron 57 (^{57}Fe). Observations of the raw data showed that many water samples contained (negative) concentrations that were below the MDL for ^{56}Fe, hence these negative concentrations were replaced with half the MDL concentration for this variable in line with the treatment process applied. Rahman et al. (2012) acknowledge that interferences from polyatomic species arising from the major ions in drinking water and interferences from polyatomic ions derived from the plasma gas, reagents or sample matrix can prevent a simple analysis. Despite the use of the collision/reaction cell of the Agilent 7500ce ICP-MS instrument used in this research, it may be inferred that some polyatomic interference was caused by $^{40}Ar^{16}O^{+}$, and therefore concentrations of ^{56}Fe reported for these samples were inaccurate.

Thomas (2002) and Iglesias et al. (2002) specifically note the interference of the $^{40}Ar^{16}O^{+}$ polyatomic species on the iron 56 isotope. Iglesias et al. (2002) examined the effect of collision and reaction gases helium and hydrogen, and found that for certain flow rates, each gas decreased background noise as well as the limit of detection for iron 56 (^{56}Fe). These authors concluded that a mixture of helium and hydrogen gas was optimal for multielement analyses, whereby the interference of $^{40}Ar^{16}O^{+}$ on ^{56}Fe was minimised, and unchanged or even improved limits of detection were observed for other elements (Iglesias et al., 2002).

For this research, the collision and reaction gases were used individually for the suite of 26 elements analysed. Therefore, the data obtained for both the longitudinal study and the 2013 sample collection demonstrate that despite the use of the Octopole Reaction System (ORS), no evidence was found to support the use of ^{56}Fe as a valid choice for the analysis of iron for this research.

However, the less abundant iron 57 isotope was also measured. This was deliberate and advantageous because there are no polyatomic species that interfere with this isotope. Consequently, it was concluded that the iron 57 concentrations accurately demonstrated the concentration of iron present in the water samples. Data for iron 56 did not provide useful information and were therefore removed from all future analyses.

Secondly, the field blank sample that underwent filtration (FBF), but not acidification (and was still treated with internal standard) showed higher than acceptable guideline values for

iron, copper, zinc, arsenic, selenium, molybdenum, cadmium, antimony, barium and lead. This is believed to be because the pH of this sample was uncontrolled (whereas all other samples were pH≤2), resulting in anomalous concentrations of several elements when analysed.

Also, a bottled water sample (B8) had excessive levels of chromium, manganese, nickel and selenium. This bottled water sample was identified as Cocobella Coconut Water and it was concluded that this product, which is 100% pure coconut water, was not suitable for analysis using ICP-MS. Chemometric analysis on samples B8 and FBF confirmed they were anomalous and they were subsequently excluded from futher analyses.

The vast majority of samples also possessed levels of iron (isotope 57) greater than that of the aesthetic guideline value of 300 µg/L, however, there is no health guideline associated with iron, and no complaints regarding taste, odour or appearance were recorded from homeowners. Elevated iron concentrations may be attributed to pipes or fixtures within the household plumbing system. Galvanised pipes, most common is houses built prior to the 1970s, are made from iron or steel and are coated with zinc; when these pipes corrode due to age, oxidised iron (rust) forms within the pipeline, contaminating and even discolouring drinking water (Gosford City Council, 2014). Steel pipes are similarly used in the water distribution system, and these pipes may also contribute to elevated iron concentrations. Because iron is vital for human health, the higher levels of iron observed in this research are not a cause for concern.

A tank water sample (TK20) and raw water from Bullocky Rest at Lake Samsonvale (BRLS), Lake Somerset (LS) and Wivenhoe Dam (WD) reported concentrations higher than the aesthetic guideline for aluminium, but again, there is no health guideline associated with aluminium, and none of these samples are consumed by members of the public. Four samples, one tank (TK22), two filtered (F14 and F22) and the aforementioned bottled water sample (B8) contained high concentrations of nickel, where the tank water sample had levels over three times the 20 µg/L health guideline. Samples T22, T64, F31, TK19, TK31 and the acidified field blank sample (FBA), contained concentrations of copper higher than the aesthetic guideline, while T22 and F31 copper concentrations exceeded the health guideline of 2000 µg/L.

High copper concentrations indicate that the samples collected were from homes built prior to the late 1980s, when copper pipes were prominently used for plumbing (PropEx Services LLC, 2002-2005). Comparison to Table 6-2 and Table 6-3 in Appendix C-2 shows

that these samples were in fact collected from homes built in the 1980s and/or with visible copper pipes. It is important to note that it is not uncommon for many newer houses to still use copper pipes for the hot water system, and PVC pipes for sewage and grey water. Additionally, brass faucets, valves and fittings may contribute to the copper levels in drinking water, as brass is composed of copper and zinc. The copper present in the tank water samples may be attributed to copper roofing materials or copper guttering (Block, 2009).

A single tank water sample (TK9) contained over 4000 µg/L of zinc, where the aesthetic guideline is set at 3000 µg/L, however, this water is not consumed by the homeowners and there is no health guideline associated with zinc. The use of zinc metal is common among roofing materials (Block, 2009), for galvanising for protection of other metals such as iron, and in products like Zincalum® from BlueScope Steel (Environmental Health Committee (enHealth), 2011). Therefore, because tank water is a collection of rainwater that falls on the roof, it is plausible to attribute high levels of zinc to such roofing materials.

The Oxley Creek raw water sample contained three times the acceptable concentration of arsenic, with the health guideline set at 10 µg/L. Two tank samples, TK9 and TK12 contained approximately 7 µg/L and 2.5 µg/L of cadmium, exceeding the health guideline of 2 µg/L. These exceedences are not concerning as these water samples are not being consumed as drinking water. A possible explanation for excess levels of cadmium in tank water could be due to the cadmium found in welding rods (Workplace Health and Safety Queensland, 2012) and solders used in the construction of tanks.

A total of 25 samples, tap, tank and filtered water alike reported lead levels above the health guideline of 10 µg/L. The high lead levels in the tank water samples are likely because of the use of lead nails, lead flashing or lead-based solder for pipe joints. It is known that lead is used in roofing nails and washers (Block, 2009), and according to enHealth (2011), roof materials and uncoated lead flashing remain a potential source of contamination. The problem can be exacerbated by poorly maintained roofs and gutters, where the water is made more acidic with organic substances from materials such as leaf litter. Similarly, rain water itself tends to be more acidic; these factors mobilise lead, and possibly other metals, into solution (Environmental Health Committee (enHealth), 2011).

Elevated concentrations of lead in tap and filtered water samples may be attributed to the use of lead solder for copper pipe joins and/or copper and brass faucet joints (Block, 2009). Block (2009) reported that experts regard the corrosion of lead solder as the major cause of

lead contamination in drinking water today. The use of lead-based solder has been banned in Australia since 1989 (The Lead Group Inc., 2013). Lead piping was popular in household plumbing systems until early in the 20th century, therefore, homes built prior to the 1930s are likely to contain lead piping (PropEx Services LLC, 2002-2005). This is not believed to be the case for these potable water samples as none of the residences visited for sample collection were built prior to the 1930s.

Overall, it can be concluded that almost all water samples collected and analysed in 2013 conform to the 2011 ADWG. Following the direct comparisons to the 2011 ADWG, the raw data of the varying sample types collected were compared to fulfil the objectives set out for this research.

4.2.4.2 Internal Raw Data Comparisons

One of the objectives of this research was to determine if there is any difference in water quality between treated water from the Mt Crosby West Bank Water Treatment Plant and tap water supplied to the consumer through the distribution system. This objective serves to answer the second part of the first research question proposed (Question I.b.) as per section 3.1.3 of Chapter Three: do the trace element and heavy metal concentrations in treated water change by the time it reaches our taps?

Simply, once treated water leaves a water treatment plant (WTP), it flows through the distribution system and onwards into the household plumbing system. Therefore, this question can be answered by directly comparing treated water and mains water, and then mains water and tap water using raw data.

Firstly, the expectation was that mains water, which was sampled from the mains distribution system around Brisbane as shown in Figure 4-20 (also see Table 6-5 in Appendix C-2), would contain higher concentrations of all trace elements and heavy metals than treated water sampled directly from Mt Crosby West Bank Water Treatment Plant. As expected, mains water contained the highest concentration of almost all elements of interest, with the minor exceptions of molybdenum, silver and uranium. Additionally, the significantly increased levels of calcium and iron may be attributed to water hardness (water containing calcium carbonate, $CaCO_3$) and the iron(III) composition of the mains water distribution pipes. Releases of built-up iron oxides (rust) due to sudden changes in mains pressure or alkalinity could similarly result in the higher levels of iron observed in the mains water samples.

Next, mains water was compared to tap water. Again, most maximum concentration values were associated with the mains water samples. Similarly, tap water samples contained higher concentrations of trace elements and heavy metals than treated water, and tap water concentrations were much closer to those observed in mains water samples.

Notably, concentrations of copper and zinc were higher in tap water samples. These results may be attributed to the copper pipes found in the majority of households in South East Queensland, as well as zinc found in galvanising materials and assorted fixtures (i.e. brass) within a household plumbing system.

Additionally, lead, iron, nickel and cobalt concentrations are similar across both mains water and tap water samples. Again, all of these elements can be found in a variety of plumbing fixtures, such as lead in brass and soldering used on pipes, nickel plating, and rust; consequently, it is not surprising that relatively high concentrations of these elements are present in tap water samples.

Finally, it is interesting to note that newer housing estates generally had lower concentrations of trace elements and heavy metals. This is believed to be due to current building trends towards using PVC pipes and joint fittings, in addition to newer mains water distribution pipes that have been laid or extended specifically for new housing estates.

The results of these internal raw data comparisons can be verified through the use of PCA, specifically when examining the relatively close relationship between tap water and mains water quality.

By examining the PCA scores plot for tap water and mains water samples, it can be seen in Figure 4-22 that the different water sources are indeed distinguishable from each other. The tap water samples dominate the left hand side, while the mains water samples are all in the lower right hand quadrant of the scores plot that represents 67.3% of the data variance.

Additionally, the PCA loadings plot depicting the trace elements and heavy metals analysed in tap water and mains water samples reinforces the observation that tap water samples generally have higher concentrations of copper and zinc, and that tap and mains water samples have similar concentrations of lead, iron, nickel and cobalt.

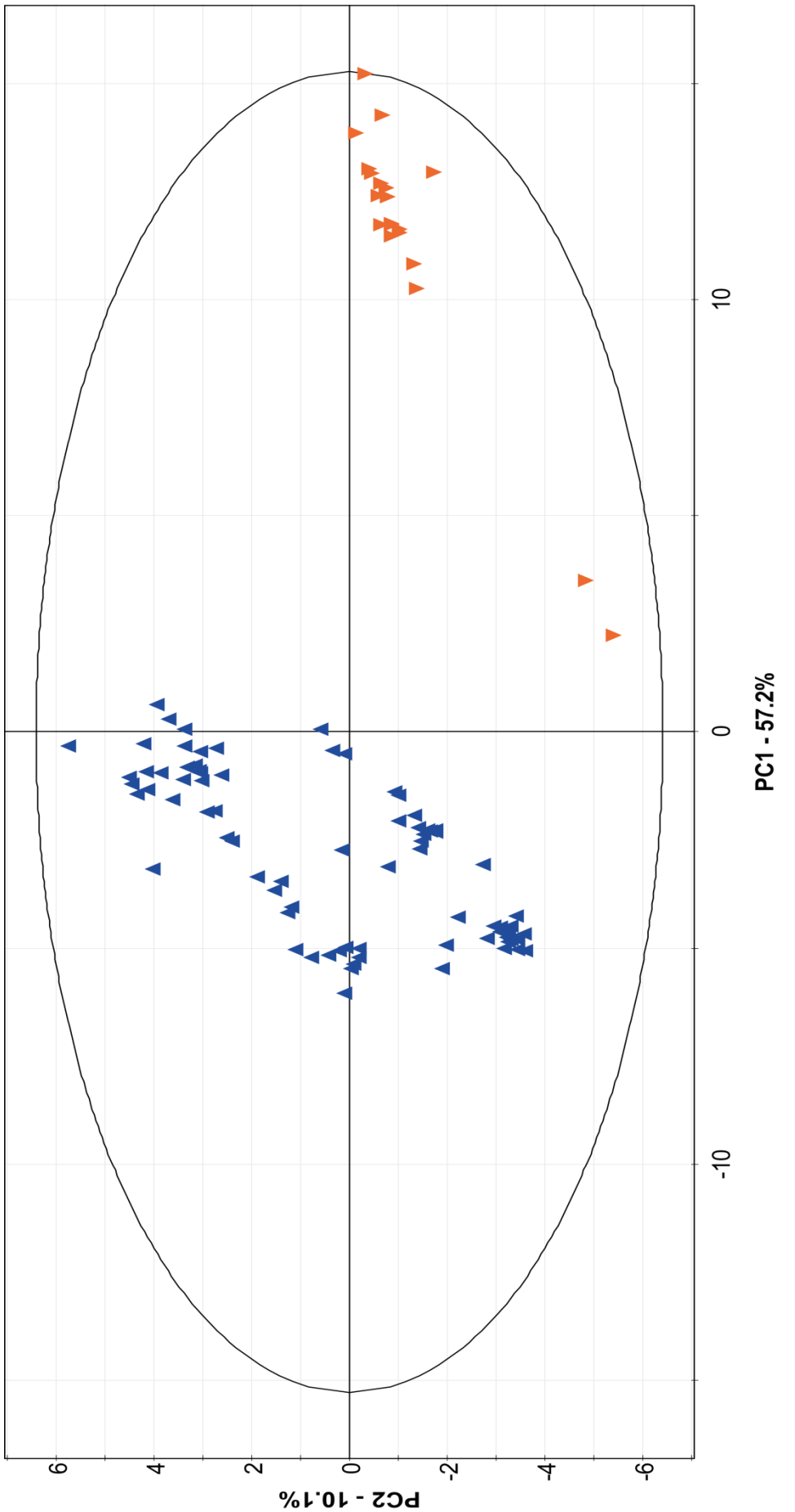


Figure 4-22. PCA scores plot displaying the relationship between the tap water and mains water samples analysed in 2013. 67.3% of total data variance is demonstrated in the first two principal components. Water samples are represented as follows: tap (T) - blue triangle and mains water (MW) - orange inverted triangle.

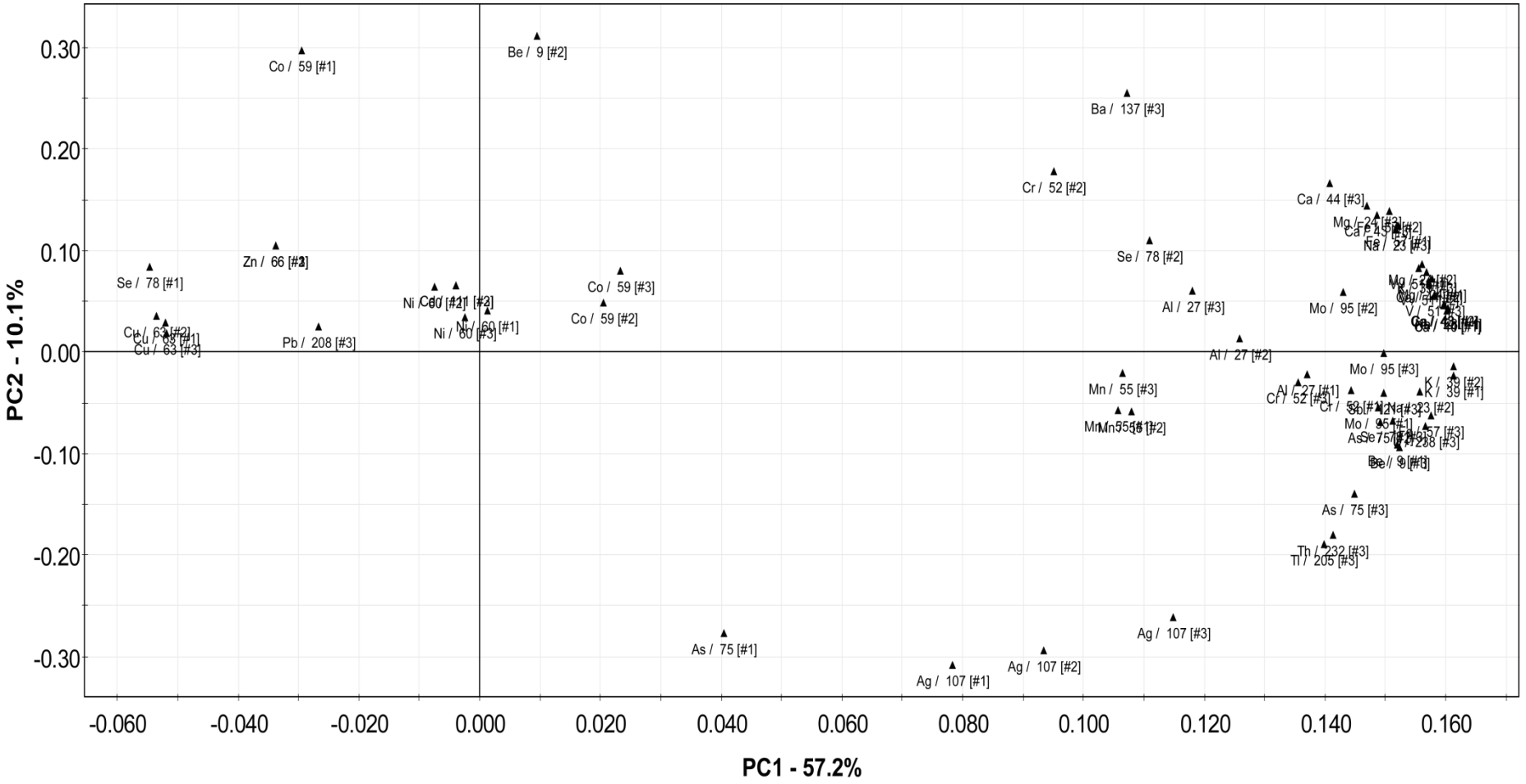


Figure 4-23. PCA loadings plot displaying all trace elements and heavy metals of interest and analysed in tandem with Figure 4-22. It similarly displays 67.3% of total data variance in the first two principal components.

Figure 4-23 shows that both copper and zinc are the elements clearly associated with tap water, as they are positioned furthest from the origin and on the left hand side of this loadings plot, like the tap water samples in Figure 4-22. Lead is similarly associated with tap water, while cobalt and nickel are located close to the origin, suggesting they possess only a small amount of variance and have similar associations with tap water and mains water. Almost all other elements are positioned on the right hand side of Figure 4-23, indicating their clear correlation to the mains water samples.

It is important to note the separation between some elements on Figure 4-23, such as that of arsenic (^{75}As) and selenium (^{78}Se). It can be inferred that this PCA loadings plot has revealed interferences that may otherwise have gone undetected. Such sources of analytical bias demonstrate random uncertainty and/or systematic errors in a useful diagnostic manner.

Consequently, it is necessary to determine which variables, i.e. which tuning steps of these elements, are likely to possess the least uncertainty and/or systematic bias, and are therefore appropriate for use in the discussion of results. Tuning steps [#1], [#2] and [#3] employed hydrogen reaction gas, helium collision gas or no gas, respectively. The interaction between the polyatomic ions and the gas in the ORS leads to the removal of interference from the mass spectrum (Agilent Technologies Inc., 2005b).

For ^{78}Se, hydrogen reaction gas is recommended to react with the Ar_2^+ (or $^{40}Ar^{38}Ar$) species by initiating a proton transfer reaction, thereby removing this interference without loss of ^{78}Se analyte signal (Wilbur et al., 2004). Similarly, helium collision gas is recommended for all analytes suffering from matrix-based interferences, such as that of $^{40}Ar^{35}Cl^+$ interfering with ^{75}As. The benefit of using helium collision gas is that this mode is universally effective, in that it removes all interferences, and since the cell gas is inert, no reaction with the sample matrix or analytes takes place and no new interferences are formed (Agilent Technologies Inc., 2005b).

Therefore, where significant separation of the tuning steps of a single trace element or heavy metal is observed in a PCA loadings plot, the tuning step recommended in the literature for interference removal will be relied upon to provide the most accurate information given by an element. For Figure 4-23, data points ^{75}As [#2] and ^{78}Se [#1] are used in any subsequent discussion of results, and all other tuning steps for these elements are included only for diagnostic and exploratory purposes.

Therefore, based on the observations of the raw data and PCA results, it can be concluded that the concentrations of the trace elements and heavy metals in the treated water analysed in this research do indeed change (increase) as a result of the waters' journey to consumers' taps.

4.2.4.3 Comparisons to Independent Water Quality Reports

As previously mentioned in Chapter One, the organisations responsible for regular water quality testing in South East Queensland are Seqwater and government organisations like Queensland Urban Utilities. The regular reports made available to the public by these organisations serve as an external point of comparison for the analysis of trace elements and heavy metals of interest. There are many facets of water quality testing and as a result, the selection of trace elements and heavy metals analysed in this research is far more extensive than those analysed by Seqwater and Queensland Urban Utilities.

The geometric means of potable water sources, tap, filtered, treated and mains water, were compared to the Monthly Seqwater Grid Report for June 2013, the month in which water samples were collected for this research, as well as to the SEQ water grid Drinking Water Quality July 2012 – June 2013 report by Queensland Urban Utilities. Scientific Analytical Services (SAS) Laboratory is the NATA accredited facility used by Queensland Urban Utilities for all chemical (and biological) analyses. Maximum, minimum and average concentration values were recorded in each of these external reports, and it was the average values that were selected for comparison against the geometric means of the potable water sources. There were several exceptions in the SEQ water grid Drinking Water Quality July 2012 – June 2013 report, where maximum concentration values were used for chromium and nickel, as the average values reported were below this laboratory's "Limit of Reporting".

Both the Monthly Seqwater Grid Report for June 2013 and the SEQ water grid Drinking Water Quality July 2012 – June 2013 report can be seen as Figure 6-31 and Figure 6-32 respectively in Appendix C-3. Of the metal ion concentrations available for comparison, the mean levels of magnesium, calcium, iron, copper, zinc and lead tested higher for this research than the independent report averages. The remaining comparable element concentrations were lower than those reported by Seqwater and Queensland Urban Utilities for these time periods.

Firstly, magnesium and calcium are multivalent cations that are commonly associated with hard water. Although the concentrations of magnesium and calcium reported for this research are elevated with respect to the concentrations detailed in the independent reports, the concentrations of both of these elements are significantly below 100 mg/L (ppm). This suggests that the waters analysed are soft waters, which have high tendencies to be corrosive to water pipes (WHO, 1996 within Ayoko et al., 2007).

In addition, the higher concentrations of iron, copper, zinc and lead can be explained by the difference in sample collection for this research and the independent water quality reports. Seqwater and Queensland Urban Utilities only obtain water samples from the mains water distribution system at street level, and do not conduct individual household analyses unless such an analysis is purchased by the homeowner. In contrast, the majority of samples for this research were collected at the tap, and a smaller number of filtered water, then mains water and finally treated water samples were also collected. Therefore, it is reasonable to conclude that the combined geometric mean of all of these potable water sources reflects the higher levels of iron, copper, zinc and lead in the potable water coming from consumers' taps. As previously stated in section 4.2.4.1, it is expected that tap and filtered water samples would contain higher concentrations of these elements due to the majority of houses in South East Queensland having copper pipes, as well as iron, lead and zinc in assorted plumbing fixtures, including brass, galvanising and rust within household plumbing systems.

For example, elevated copper concentrations indicate that the samples collected came from homes built prior to the late 1980s, when copper pipes were prominently used for plumbing (PropEx Services LLC, 2002-2005). Similarly, galvanised pipes or fittings, common is household plumbing systems prior to the 1970s, may contribute to the high levels of iron reported in potable water in this research. Because they are made from iron or steel and coated with zinc, oxidised iron (rust) forms within the pipeline when galvanised pipes corrode due to age, contaminating and even discolouring drinking water (Gosford City Council, 2014).

Additionally, elevated levels of zinc may indicate the use of galvanised pipes or fittings in the homes from which these samples were collected. Furthermore, brass, an alloy composed of copper and zinc, has many uses including pipes, faucets, valves and other fittings (Block, 2009), all of which could contribute to the excess levels of zinc in potable water samples.

Finally, lead in tap and filtered water samples in concentrations higher than those detailed in the independent reports analysed may be attributed to the use of lead solder for copper pipe joins and/or copper and brass faucet joints (Block, 2009). Block (2009) reported that experts regard the corrosion of lead solder as the major cause of lead contamination in drinking water today, even though the use of lead-based solder has been banned in Australia since 1989 (The Lead Group Inc., 2013).

Magnesium, calcium, iron and zinc are elements found naturally in water and do not have an associated health guideline. Moreover, it is important to note that none of the combined geometric means of the potable water sources, or the averages reported by Seqwater and Queensland Urban Utilities exceeded any health guidelines according to the 2011 ADWG.

The determination of basic statistics and the comparison to the 2011 ADWG, internal comparisons among raw data and external comparison to independent reports represents the limit of significant analysis that can be performed on such a large data matrix without employing multivariate statistical methods. Therefore, several chemometric techniques were applied to this data, the results of which are presented in the following sections.

4.2.5 Chemometric Analysis of 2013 Data

After extracting all possible information from the raw 2013 data, a series of chemometric techniques were employed to gain the most from these data. In the data matrix for this research, all water samples are considered objects. Concurrently, all tuning steps for all trace element and heavy metal isotopes analysed are included as individual variables in all chemometric techniques. The tuning steps recorded were [#1] hydrogen (reaction) gas, [#2] helium (collision) gas and [#3] no gas. As a result, there are three concentrations for each trace element and heavy metal isotope analysed that are all considered variables in this research.

Exploratory data analysis in the form of Principal Component Analysis (PCA) is arguably the best tool for elucidating underlying patterns within a data matrix, as demonstrated in Chapter Two. Used in tandem with PCA, complementary technique Hierarchical Cluster Analysis (HCA) gives further evidence to observations originating from PCA results. For both of these techniques, the objects were the water samples collected, and the variables were all trace elements and heavy metals analysed.

Additionally, multicriteria decision making methods Preference Ranking Organisation METHod for Enrichment Evaluation (PROMETHEE) and Graphical Analysis for Interactive Assistance (GAIA) were used to determine which raw water sources (dam and lakes across South East Queensland) were most preferred.

Temporal variations in potable water quality will also be analysed through the use of PROMETHEE and GAIA, along with the corresponding climatic conditions of each year of this longitudinal study, to determine if changing climatic conditions have an effect on water quality. Finally, PLS analysis will be used to investigate whether metal ions possess predictive ability and are therefore capable of being predictors for water quality.

4.2.5.1 Principal Component Analysis (PCA) of All Water Sources

As explained in section 4.1.3, all variables were mean centred and scaled to unit variance when the data matrix for samples collected in 2013 was imported into the SIMCA-P 10.0 software (Umetrics AB, 2005b).

Firstly, all sample data were plotted together using PCA in an attempt to detect any obvious patterns present. Therefore, Figure 4-24 includes all water samples collected for analysis in 2013. 63.3% of total data variance is depicted, and almost all samples lie within the Hotelling T2 95% confidence ellipse. The three outliers not visible on Figure 4-24 are the filtered field blank (FBF), bottled water sample B6 and the raw water sample from Oxley Creek (OC). These outliers were removed from further analysis.

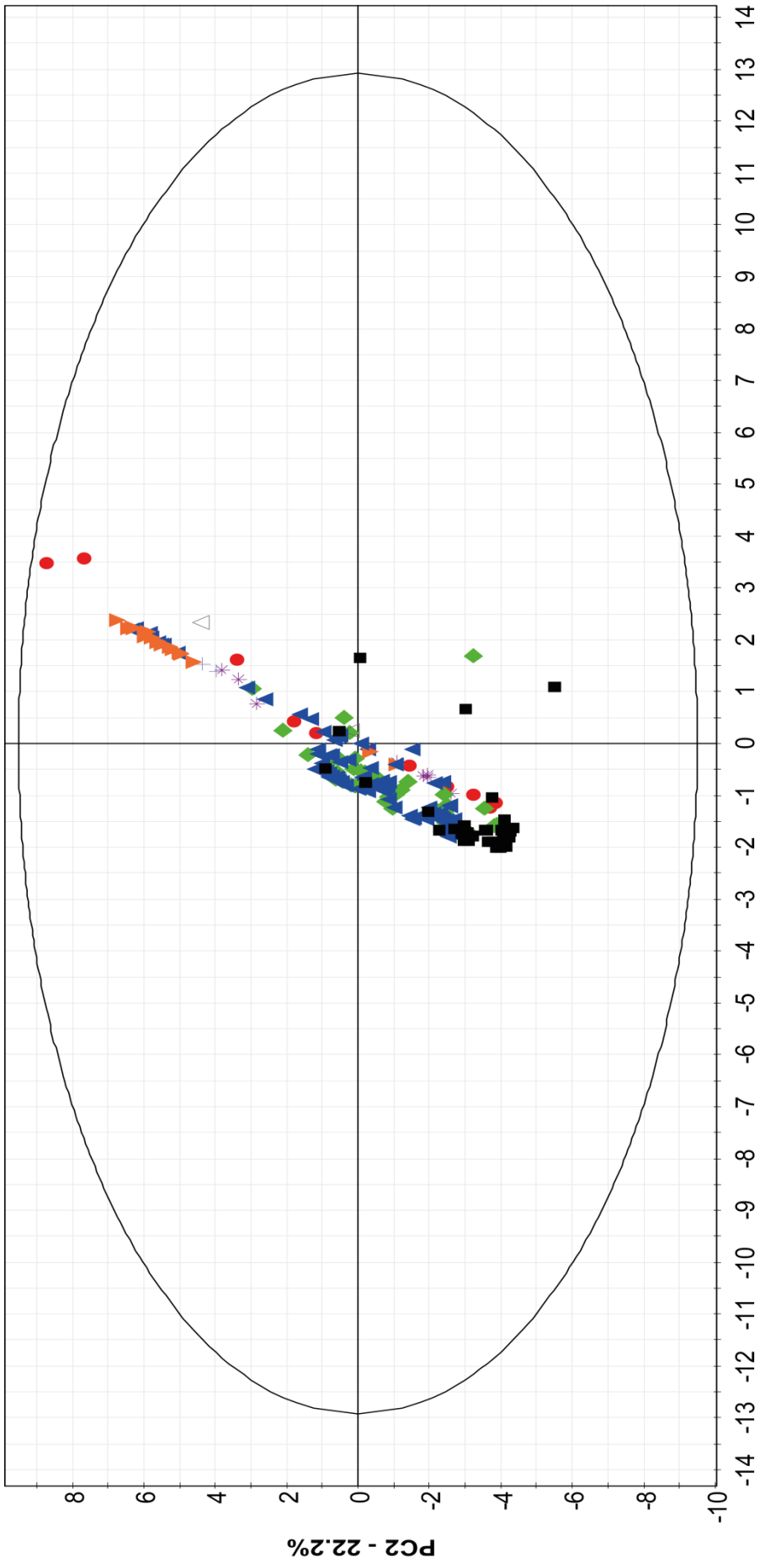


Figure 4-24. PCA scores plot explaining 63.3% of data variance and displaying all water samples collected in 2013. Almost all water samples lie within the Hotelling T2 95% confidence ellipse depicted here. Water samples are represented as follows: tap (T) - blue triangle, filtered (F) - green diamond, tank (TK) - black square, bottled (B) - red circle, mains water (MW) - orange inverted triangle, raw water - purple star, treated water - blue-grey cross, trip and field blanks - grey open triangle.

Figure 4-24 shows the tap, tank and filtered water samples clustered closely and on top each other, as are some bottled water samples. The mains water, raw and treated water samples can also be seen stretching away from the central cluster. It was impractical to perform HCA on the large number of samples plotted in Figure 4-24, as the dendrogram would be illegible.

Such a large amount of data displayed on one PCA plot significantly limits the conclusions that can be drawn. Therefore, to more clearly observe the patterns emerging in the data, the different water sources analysed were plotted separately and in numerous smaller combinations.

For all of these combinations, mercury was removed due to the erroneously high concentrations reported for this variable. Additionally, ^{56}Fe was removed from analysis due to inaccurate results attributed to polyatomic interferences; however, ^{57}Fe was also analysed and used as a viable alternative, as stated in previous section 4.2.4.1.

4.2.5.2 PCA of Raw and Potable Water Sources

Determining if it is possible to distinguish heavy metal fingerprints of various water sources will answer the first question proposed in this research. This research question can be answered using a combination of PCA and HCA analyses that show the separation of the different water sources collected for this research.

The first part of this question (Question I.a.), as per section 3.1.3 of Chapter Three, asks if raw water is distinguishable from treated water. Two treated water samples from Mt Crosby West Bank WTP were collected directly from each of the reservoirs on Cameron's Hill. For the purposes of answering this research question, the tap water samples collected will also be considered as water that has been treated, as the public who regularly consume their tap water trust that it has been appropriately treated and tested by the responsible authorities, in this case, the Mt Crosby West Bank WTP, Seqwater and Queensland Urban Utilities.

Figure 4-25 therefore includes raw water, treated water and tap water samples collected in 2013. Tap water samples H2-19, the trip blank and two field blanks were removed as outliers, as was the Oxley Creek raw water sample. As stated previously in section 4.2.4.1, mercury and iron 56 were also removed from this analysis.

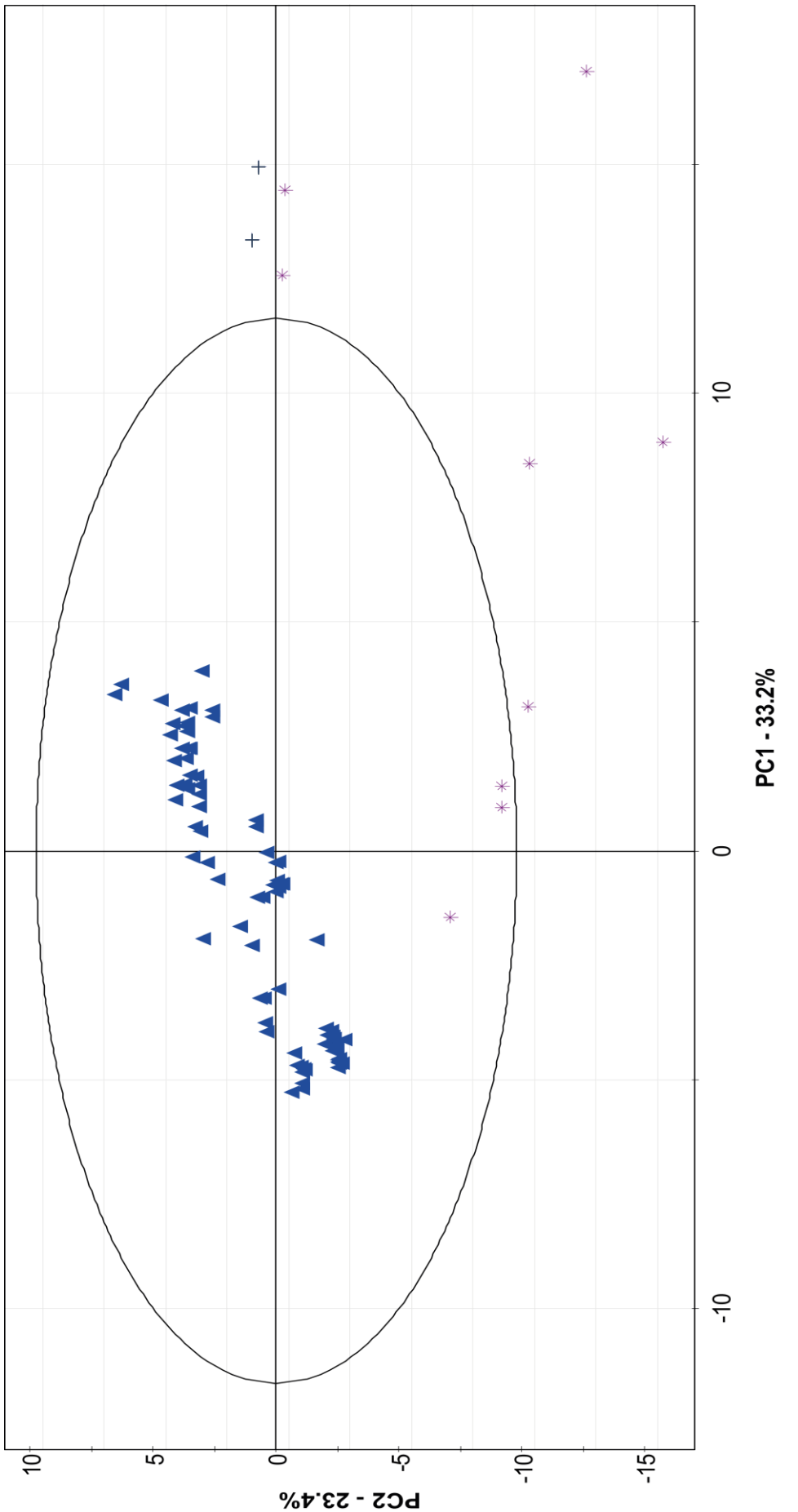


Figure 4-25. PCA scores plot displaying 56.6% of total data variance for tap, raw and treated water samples collected in 2013. Water samples are represented as follows: tap - blue triangle, raw - purple star, treated – blue-grey cross .

The treated water samples from the reservoirs on Cameron's Hill can be seen in the top right hand positive quadrant of Figure 4-25, closely correlated with two raw water samples. These raw water samples were collected from the Mt Crosby West Bank WTP and from College's Crossing, four and a half kilometres downstream from this WTP. Hence it is reasonable that these four samples form a cluster because they were all collected from the same geographic area.

Additionally, the majority of raw water samples (purple stars) are positioned outside of the Hotelling T2 95% confidence ellipse. This result is justifiable considering the raw water samples were collected directly from dams, lakes, rivers and creeks, and had not undergone treatment of any kind. It can easily be argued that raw water should indeed be significantly different to tap water that has undergone rigorous treatment to meet the 2011 Australian Drinking Water Guidelines, to the extent that, when analysed simultaneously by PCA, raw water appears as an outlier in comparison to treated tap water.

From these observations, it can be concluded that raw water is easily distinguishable from treated water based on the trace element and heavy metal fingerprints of these different sources (Question I.a.).

Futhermore, Question I.d. asks if raw water source determination is possible using the trace metal profile of a potable water sample. It is known that water from the majority of raw water sources analysed here is mixed when treated at Mt Crosby West Bank WTP and within the water distribution system. Therefore, it was not expected that any single raw water sample would match potable water samples from a particular area.

In order to answer Question I.d., tap water was first analysed alone to determine if sample collection locations had an effect on the quality of water. Tap water samples T83-86, H2-19, the trip blank and two field blanks were removed as outliers. Similarly, tuning steps for beryllium and cadmium (^{9}Be [#1 and #3] and ^{111}Cd [#1]) were removed by SIMCA-P 10.0 for possessing little to no variance.

Figure 4-26 displays the clustering of tap water samples according to suburb groups (several outliers have been excluded). The eight clusters highlighted on this scores plot correspond to Figure 4-27, a map that depicts matching suburb areas from which samples were collected.

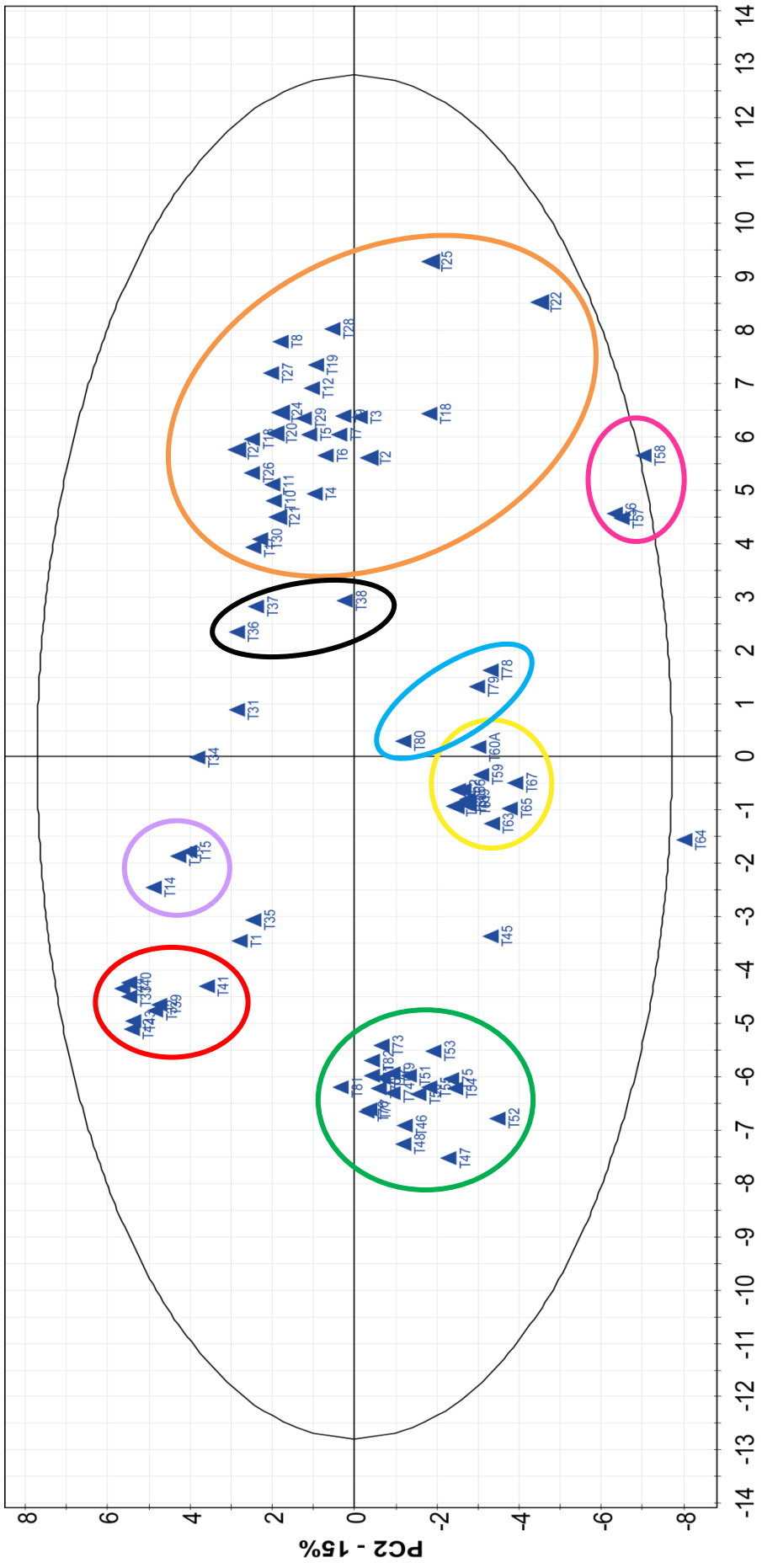


Figure 4-26. PCA scores plot showing tap water samples. 56.2% of total data variance is described. Each coloured circle represents a suburb cluster and corresponds to Figure 4-27.

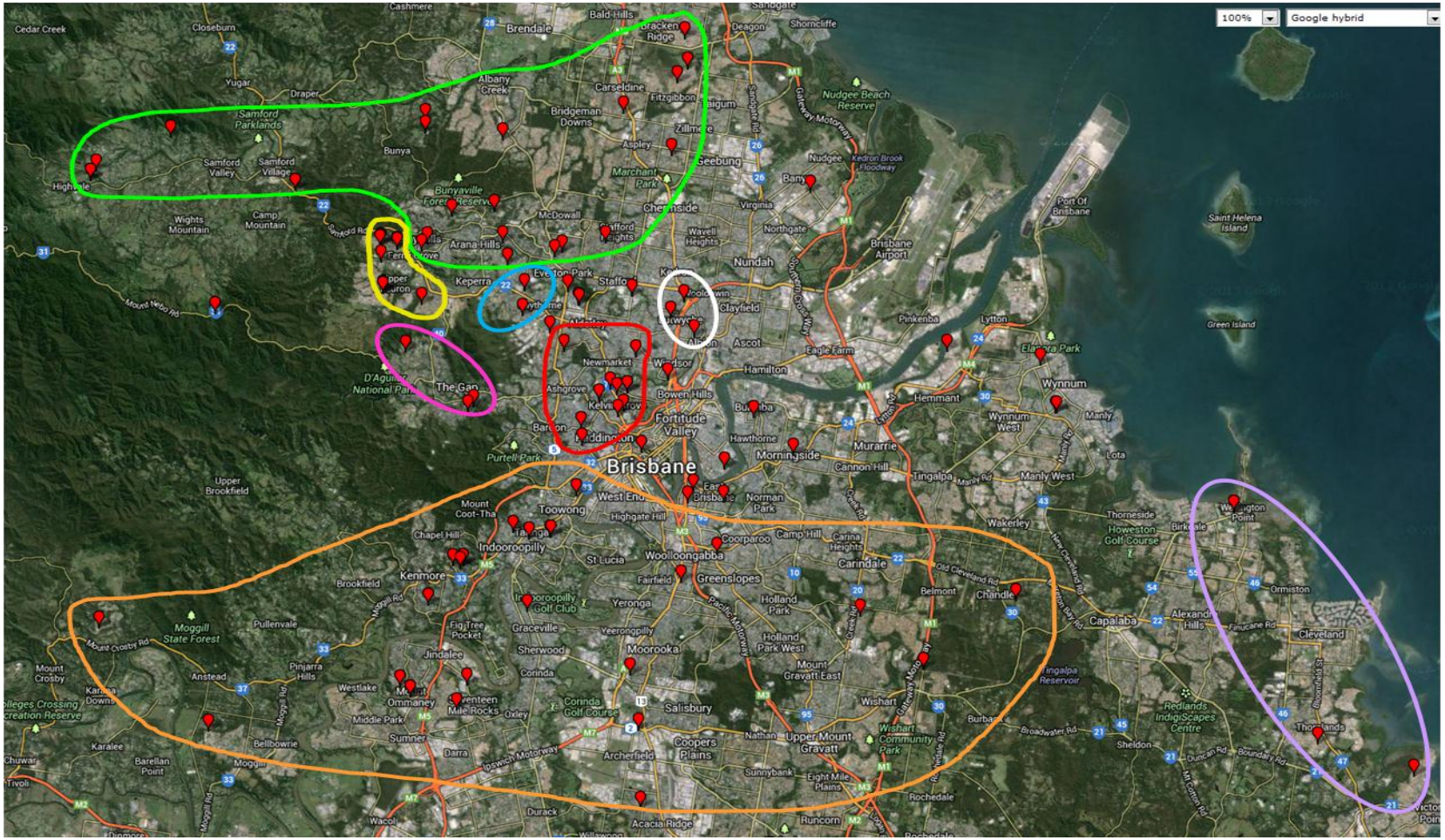


Figure 4-27. Map showing the residences from which tap water samples were collected. Suburb areas highlighted match clusters outlined in Figure 4-26. The black and white circles on Figure 4-26 and Figure 4-27 respectively correspond to Lutwyche.

Same colour clusters highlighted on both Figure 4-26 and Figure 4-27 indicate neighbouring suburbs in areas around Brisbane. The green cluster represents Bracken Ridge, Fitzgibbon, Carseldine, Aspley, Albany Creek, Bunya, Samford, Highvale, Ferny Hills, Arana Hills, Everton Hills and Everton Park. The yellow cluster groups Ferny Grove, Keperra and Upper Kedron.

The blue cluster pairs Mitchelton and Gaythorne, the pink cluster includes samples taken from areas within The Gap, and the red cluster groups the numerous samples taken from Kelvin Grove, Red Hill and Alderley.

The black cluster on Figure 4-26 and the white cluster on Figure 4-27 represent different residences within Lutwyche. The purple cluster consists of three suburbs east of Brisbane: Thornlands, Victoria Point and Wellington Point.

Finally, the large orange cluster incorporates Shalier Park, Acacia Ridge, Mt Ommaney, Bellbowrie, Graceville, Indooroopilly, Mansfield, Taringa, Toowong, Chapel Hill, Annerley, Greenslopes, East Brisbane, Bulimba, Morningside and Wynnum.

The fact that tap water samples from similar suburb areas cluster accordingly indicates that water quality in specific areas of South East Queensland is characteristic of that area. It can be inferred that the similarities in water quality for each of these suburb areas may be influenced by the age of the development of suburb and therefore the age of the water distribution pipes in that area, as well as the distance the treated water has travelled from the Mt Crosby WTP to each suburb.

Additionally, qualitative information obtained from the survey of homeowners showed that residents of some areas believe that their potable water originates from specific dams and the associated water treatment plants. For example, residents of Samford, Highvale and surrounding areas (the Pine Rivers region) believe that they are supplied with water from North Pine Dam (Lake Samsonvale) treated at the North Pine Dam WTP.

Seqwater states that North Pine Dam and North Pine Dam Water Treatment Plant supplies many northern Brisbane suburbs as well as regions of Moreton Regional Council including Pine Rivers, Caboolture and Redcliffe City (Seqwater, 2011). Similarly, residents in The Gap were formerly supplied with water from Enoggera Dam.

This exploratory PCA method allows the aforementioned conclusions regarding the distinction of water quality according to suburb areas; however, these conclusions represent the limit of classification achievable due to the constant mixing of all of South East Queensland's raw water sources. The general transport of water throughout South East Queensland is exemplified in Figure 4-28.

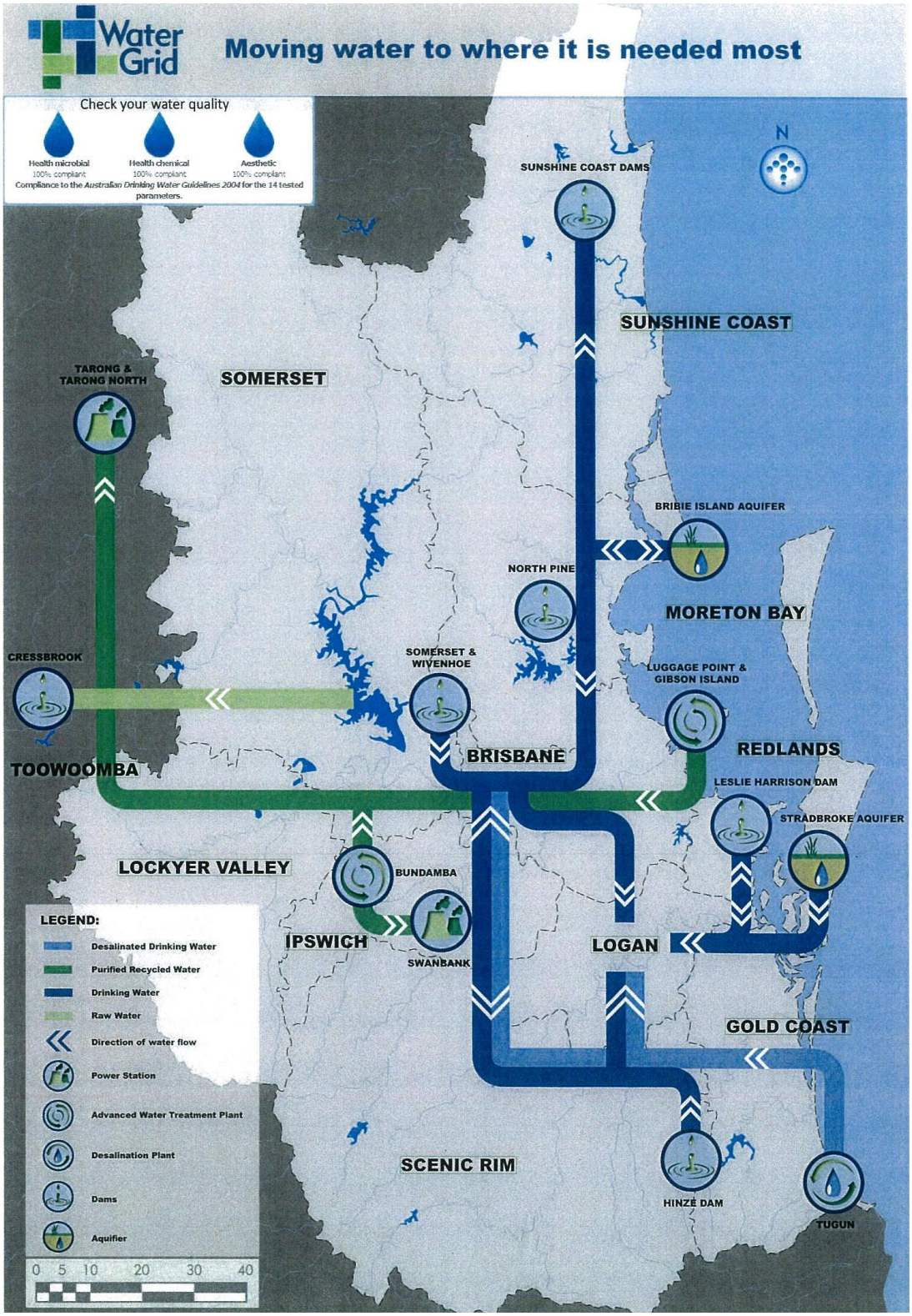


Figure 4-28. South East Queensland's Water Grid and the movement of water throughout the region. Drinking water is distinguished by the dark blue lines, and the arrows denote the direction of water flow (SEQ Water Grid Manager, 2012). Reprinted from SEQ Water Grid Manager Annual Report 2011-12, p. 10, Copyright (2012), with permission from Seqwater.

Figure 4-28 shows the centralised nature of water distribution to the greater Brisbane area. As a result, the origin of potable water sources cannot be determined beyond the identification of suburb areas, as demonstrated in Figure 4-26 and Figure 4-27. It is believed that area classification via PCA would provide more pertinent information if this method were applied to a city like Paris, where water distribution is the individual responsibility of each municipality, and over 15,000 water treatment plants throughout the country service the population.

Overall, the patterns observed in Figure 4-26 and Figure 4-27 demonstrate the clustering of samples based on location. However, the significant difference between raw and potable water samples was established in Figure 4-25, where none of the raw water samples are shown to be related to the treated water samples. In addition to this, raw water mixing and the transport of drinking water throughout South East Queensland shown in Figure 4-28, means that raw water from an individual dam (and the associated water treatment plant) cannot be distinguished as the single supply to one area, or distinguished within the mixture of water in the distribution system. Therefore, it is not possible to determine the original raw water source using the trace metal profile of water samples collected at the consumers' tap in this research (Question I.d.).

4.2.5.2.1 Qualitative Data in Tap Water Analysis

In addition to these quantitative data resulting from ICP-MS analysis, qualitative data were also collected in the form of a brief homeowner survey detailed in section 3.4.1.1. Residents were asked about their knowledge of their household plumbing system and the various ways in which their water was used. The age of the home and the composition of household pipes were facts that the majority of residents knew. Where the composition of the household pipes was not known, the following assumptions were made based on previous research and on construction practices: homes built in the late 1980s and onwards were assumed to have plumbing systems constructed mainly of PVC pipes; homes built prior to the late 1990s had copper plumbing systems. There were also residents that knew neither the age of the home nor the composition of the household plumbing system.

Consequently, this qualitative survey data were converted into quantitative data by adding each pipe type as a categorical variable to the existing set of trace element and heavy metal variables for all tap water data. Each pipe variable can be considered categorical because there is no intrinsic ordering to any of the three categories.

Pipe types were divided into three separate categorical variables: PVC pipes, copper pipes or unknown. If a home had copper pipes, '1' was entered into the copper pipes variable column, and '0' was entered into both the PVC pipes and unknown columns; similarly, a tap water sample coming from a home that had PVC pipes contained a '1' in the appropriate column, while a '0' was entered into both the copper pipes and unknown columns. This process was continued until all tap water samples had been categorised as having come from PVC pipes, copper pipes or an unknown composition of pipes.

PCA was then performed on the tap water data including the categorical pipe variables. Mercury and iron 56 were removed from this analysis as it has previously been demonstrated that the results for these elements were anomalous. Figure 4-29, the PCA loadings plot for all variables, displays the positioning of the individual pipe types in relation to the origin and all trace element and heavy metal variables.

Both the PVC pipes and copper pipes variables are located in the upper left hand quadrant of Figure 4-29. Lead, copper, zinc and nickel are the heavy metals that appear in the same quadrant and are therefore associated with tap water samples from both PVC and copper pipes. This is a reasonable result because copper pipes will obviously contribute to copper concentrations in the water samples; lead, zinc and nickel can be found in soldering used on pipes, galvanising and tap fittings. Cadmium, also visible close to the origin, is sometimes found in the coating of the welding electrode or other protective coatings, can be present as impurities in galvanised fittings, and is a by-product of the welding process (Department of Commerce WA, 2013).

It may be argued that these elements are more closely associated with tap water samples from PVC pipes, however, the copper pipes variable has the longer vector (from the origin), demonstrating greater variance, and therefore the significance of the influence of copper pipes on these heavy metals is greater.

Finally, the Pipes Unknown variable is in direct opposition to both the PVC Pipes and Cu Pipes variables. None of the residences visited for sample collection in the course of this research were particularly old houses or apartment blocks. Therefore, it is logical to assume that, despite residents not knowing the age of their home or the composition of their water pipes, all tap water samples collected from the greater Brisbane area came from PVC or copper pipes.

This assumption is reinforced by Figure 4-29, where it can be seen that the vector associated with the Pipes Unknown variable perfectly intersects both the PVC Pipes and Cu Pipes variables. As a result, it can be concluded that tap water samples categorised in the Pipes Unknown variable consist of an approximately equal contribution of samples from PVC pipes and from copper pipes within the household plumbing system.

Overall, the combined use of qualitative and quantitative data collected for this research allows greater insight into the tap water samples collected, and the influence household plumbing systems can have on drinking water quality.

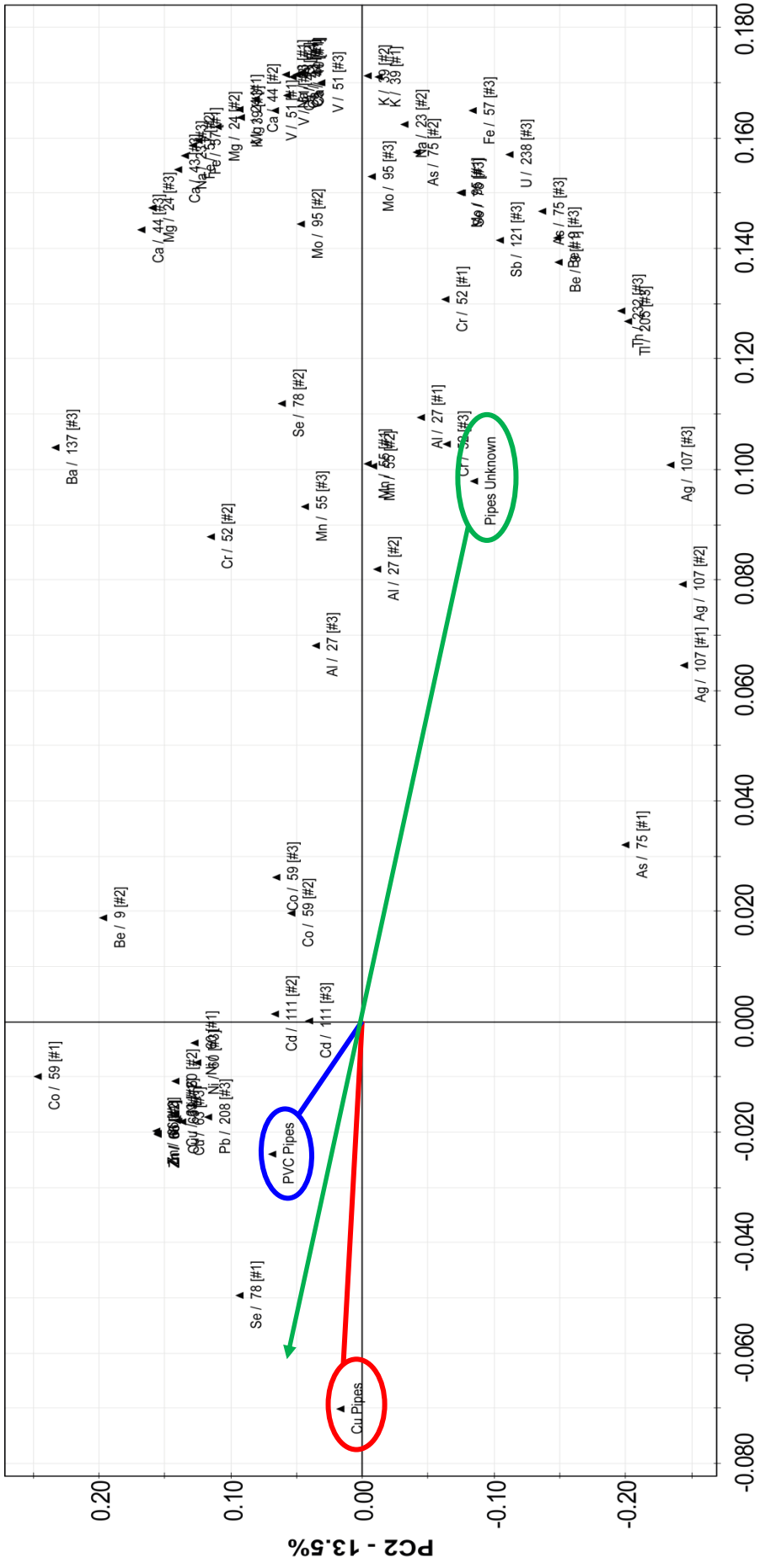


Figure 4-29. PCA loadings plot showing all variables, including pipe type, associated with the tap water samples collected for this research in 2013. 59.9% of total data variance is demonstrated within these first two principal components.

It has been firmly established that while the raw water source cannot be determined from potable water, raw and treated water can indeed be distinguished. The third part of the first research question (Question I.c.), as per section 3.1.3 of Chapter Three, asks if different potable water sources can be distinguished. Potable water samples collected for the purposes of this research include tap water, filtered water, tank water and bottled water. This question was again answered using Principal Components Analysis.

4.2.5.2 PCA of Potable Water Sources

In addition to investigating tap water independently as well as the relationship between tap and raw water, the filtered water samples collected were examined in comparison to the tap water samples. For this analysis, tap water samples T83-86, H2-19, the trip blank and two field blanks were removed as outliers, as was filtered water sample F45. Mercury and iron 56 were removed as anomalous elements, and two tuning steps for beryllium (^{9}Be [#1 and #3]) were removed by SIMCA-P 10.0 for possessing little to no variance. Figure 4-30 demonstrates the relationship between the tap and filtered water samples collected in 2013.

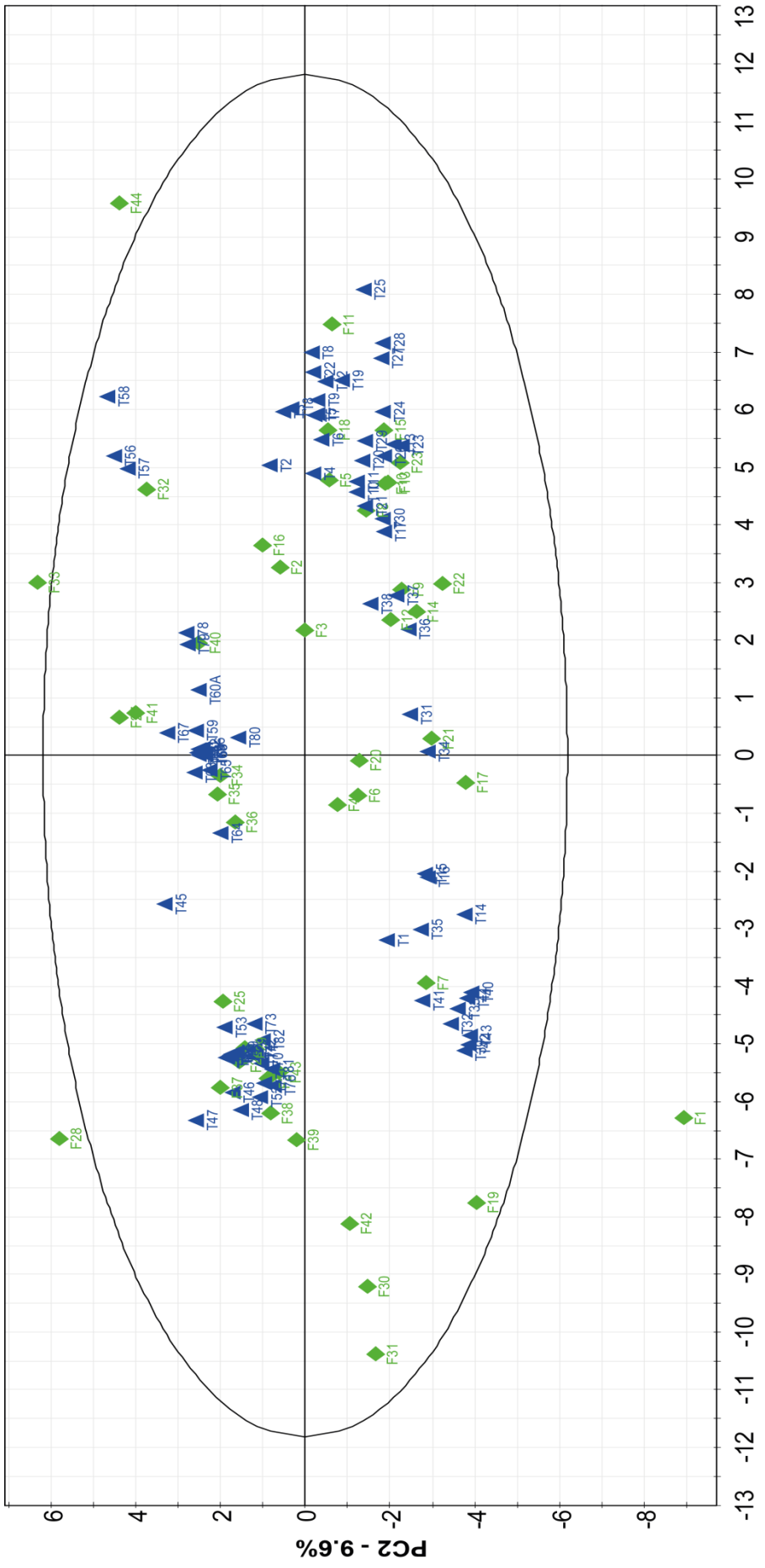


Figure 4-30. PCA scores plot depicting tap water and filtered water samples. 44.7% of total data variance is shown. Water samples are represented as follows: tap (T) - blue triangle; filtered (F) - green diamond.

Figure 4-30 displays the same tap water clusters that were identified in Figure 4-26, and many of the additional filtered water samples are observed overlaying the existing tap water clusters. The corresponding sample numbers, T# and F#, and the collection locations of samples discussed can be referenced against Table 6-2 and Table 6-3 in Appendix C-2.

There is a smaller amount of data variance (44.7%) explained by this scores plot than was explained in Figure 4-26. Therefore, less information is contained in this scores plot, and this is believed to be attributable to the larger number of objects (samples) being interpreted.

The relationship between the tap and filtered water samples is apparent, and both potable water types are observed in close proximity. Analysis using PCA demonstrates the perceptible difference between these potable water sources, as the filtered water samples can be seen slightly separate from the tap water samples, thereby distinguishing them as different and individual samples.

When tap and filtered water samples are collected from the same residence, it is clear that these sources of drinking water are strongly related. For example, samples T57 and F32 both originated from the same household in The Gap and can be seen very close together in the upper right hand quadrant of Figure 4-30, indicating that they are closely related.

This is a logical conclusion because all filtered water samples collected (with the exception of F1, F19, F30 and F31) were known to traverse the same household plumbing system as the tap water samples, whereby the only difference in the path of these samples involved the filter (usually) positioned at the end of plumbing system. There were several different kinds of filters encountered during sample collection. These included separate filter taps on sinks, filters as tap attachments, fridges with filtration systems or specialised jugs (e.g Brita®).

Filtered water samples F1, F19, F30 and F31 are exceptions to this explanation because these samples were collected from homes in semi-rural areas not supplied with town (tap) water. Accordingly, these homes contained sophisticated filtration systems to purify their own tank water for everyday use.

The relationship between tap and tank water samples was investigated in addition to the relationship between tap and filtered water.

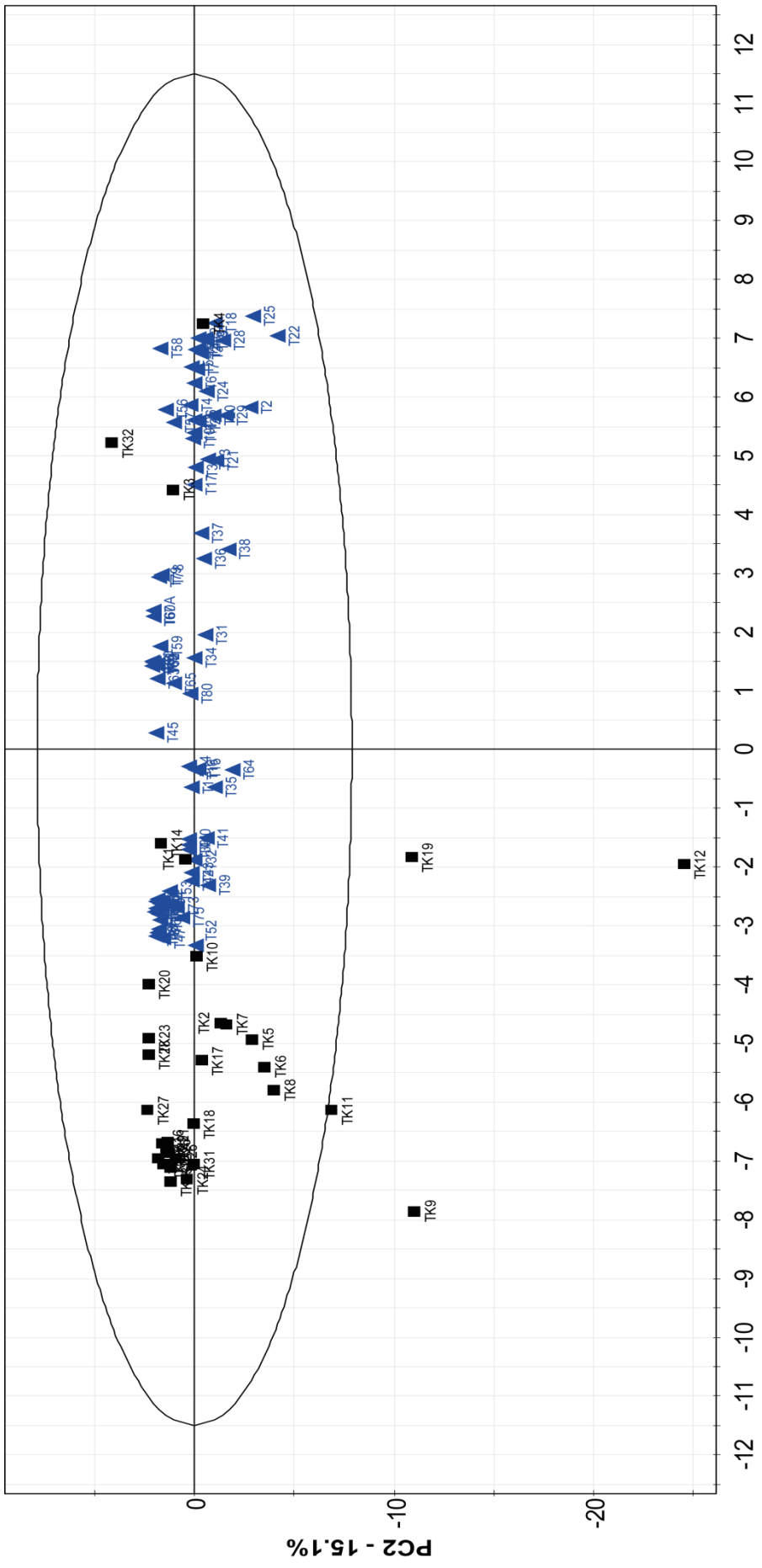


Figure 4-31. PCA scores plot displaying tap and tank water samples. 47.2% of total data variance is shown. Water samples are represented as follows: tap (T) - blue triangle; tank (TK) - black square.

Again, tap water samples T83-86, H2-19, the trip blank and two field blanks were removed as outliers in this analysis. Elements mercury and iron 56 were also removed, as they have previously been shown to be anomalous.

The same tap water clusters seen in Figure 4-26 have been compressed but are still distinguishable in Figure 4-31. In Figure 4-31, all tank water samples collected are displayed in addition to the tap water samples. The corresponding sample numbers, T# and TK#, and the collection locations of samples discussed can be referenced against Table 6-2 and Table 6-3 in Appendix C-2.

This PCA scores plot, showing 47.2% of the total data variance, displays the significant separation of the tap and tank water samples, in contrast to the close relationship observed between the tap and filtered water samples in Figure 4-30. Almost all tank water samples are positioned on the left half of Figure 4-31.

The segregation of these water sources is plausible considering the different path travelled by each source. For instance, tap water is treated, sent through the mains distribution system, then a household plumbing system before it is consumed. Alternatively, tank water is rainwater that has fallen onto rooves and flows down gutters before residing in a metal, plastic or concrete water tank. The contrast between the origins of these water sources is therefore reflected in the distinction of each type in Figure 4-31.

Information regarding the trace elements and heavy metals that are associated with tap and tank water sources can be learnt from Figure 4-32, the PCA loadings plot corresponding to this scores plot.

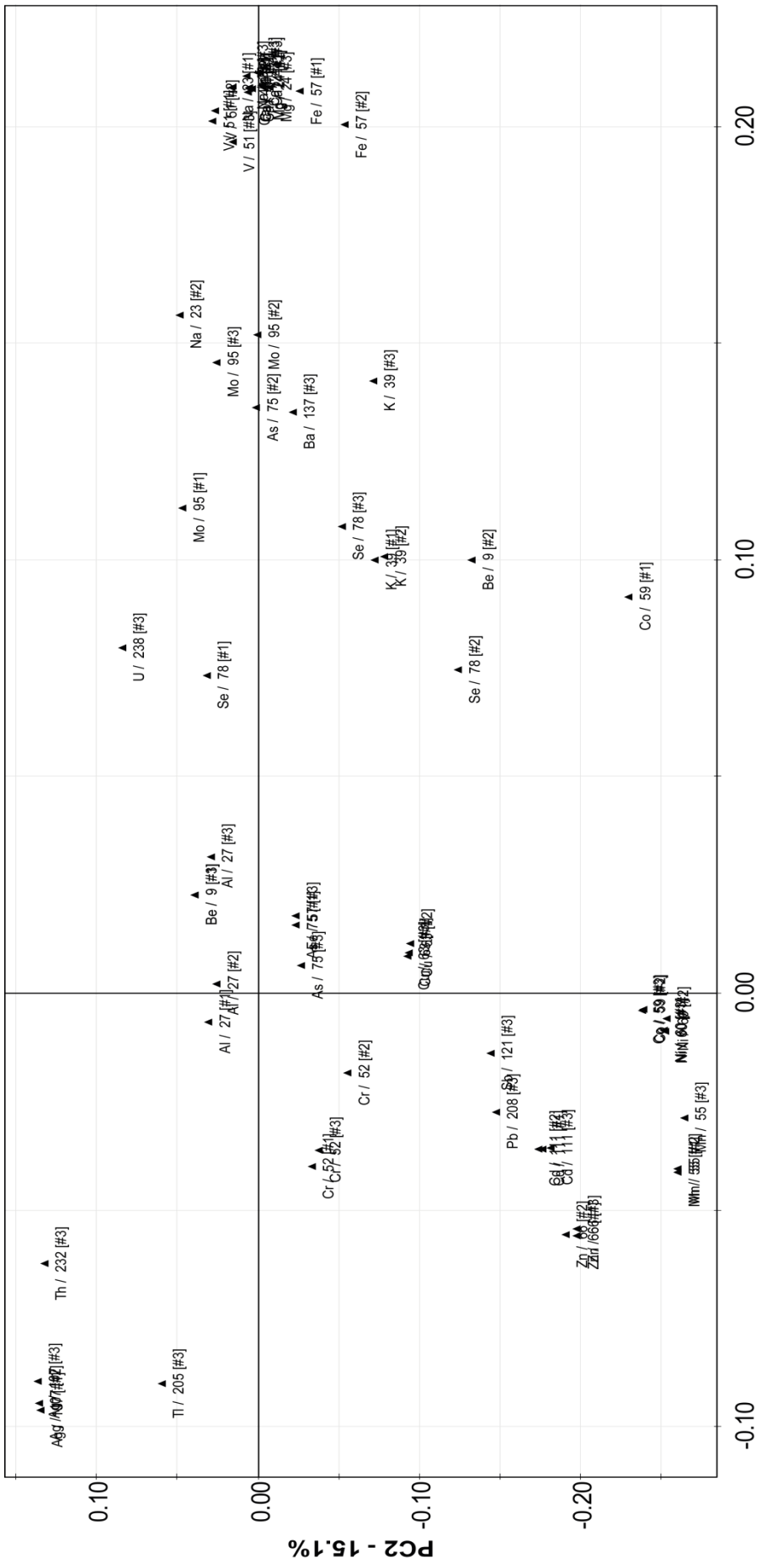


Figure 4-32. PCA loadings plot for tap and tank water corresponding to Figure 4-31. 47.2% of total data variance is displayed.

When Figure 4-31 (the scores plot displaying the tap and tank water samples collected) and Figure 4-32 (the corresponding loadings plot displaying the trace elements and heavy metals analysed) are examined together, inferences regarding element association with water type can be made.

Figure 4-32 shows that tap water is affiliated with macroelements such as iron, sodium, calcium, potassium and magnesium. Their distance from the origin of this loadings plot suggests that these elements are strongly associated with the tap water samples. Other elements, like aluminium, arsenic and copper, are very close to the origin and so are only weakly associated with tap water.

In contrast, elements appearing on the left half of this loadings plot are associated with tank water and include manganese, zinc, lead, silver, chromium, cadmium, cobalt and nickel. As previously stated in section 4.2.4.1, the use of zinc and lead is common among roofing materials, and these metals can also be found in galvanising, nails, lead flashing, or lead-based solder for pipes. Additionally, chromium can be a by-product of the welding process as it is sometimes found in the coating of the welding electrode or in other protective coatings, and it can also exist as an impurity in galvanised zinc products.

The differing abundance of the various trace elements and heavy metals in these water sources explains the distinction between sources as seen in Figure 4-31.

Finally, the relationship between commercial bottled waters and the tap water collected is examined to round out the potable water sources analysed in this research. Tap water samples T83-86, H2-19, the trip blank and two field blanks were removed as outliers, and as previously stated in section 4.2.4.1, elements mercury and iron isotope 56 were also removed.

In total, 11 bottled water brands were investigated. Bottled water samples B6 and B8 were shown to be outliers, and were consequently removed from Figure 4-33. The corresponding sample numbers, T# and B#, and the details and collection locations of samples discussed can be referenced against Table 6-2, Table 6-3 and Table 6-6 in Appendix C-2.

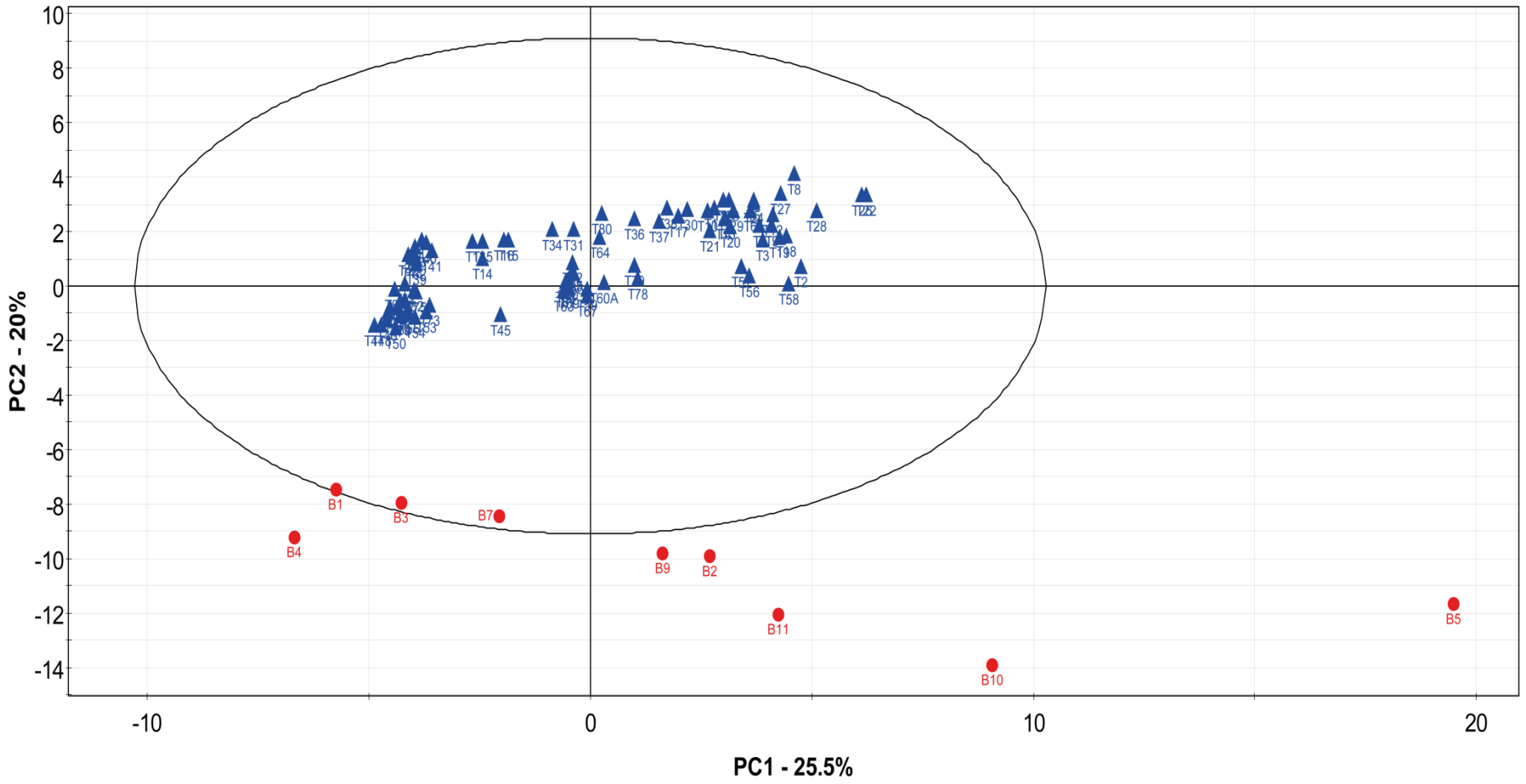


Figure 4-33. PCA scores plot displaying the relationship between the tap and bottled water samples, excluding samples B6 and B8. 45.5% of total data variance is shown in the first two principal components. Water samples are represented as follows: tap (T) - blue triangle; bottled (B) – red circle.

As previously explained in section 4.2.4.1, bottled water sample B8 was identified as Cocobella Coconut Water. It was inferred that this product, which is 100% pure coconut water, was not suitable for analysis using ICP-MS as anomalous levels of chromium, manganese, nickel and selenium were reported. Bottled water sample B6 was from the brand San Pellegrino, a lightly carbonated water, and was also an outlier. These samples were excluded from Figure 4-33.

Figure 4-33 displays 45.5% of total data variance for tap and bottled water samples. Almost all bottled water samples are positioned outside of Hotelling T2 95% confidence ellipse and are shown as outliers when compared to the tap water samples. These samples are not truly considered outliers, but they are believed to be displayed in this way because of the variation in location from which the water for each bottled water brand was sourced. Some brands tested are Australian, whilst others such as Santa Vittoria (B10) and evian® (B5) originate from Italy and France respectively.

The elements primarily associated these bottled water samples can be understood from Figure 4-34, the PCA loadings plot.

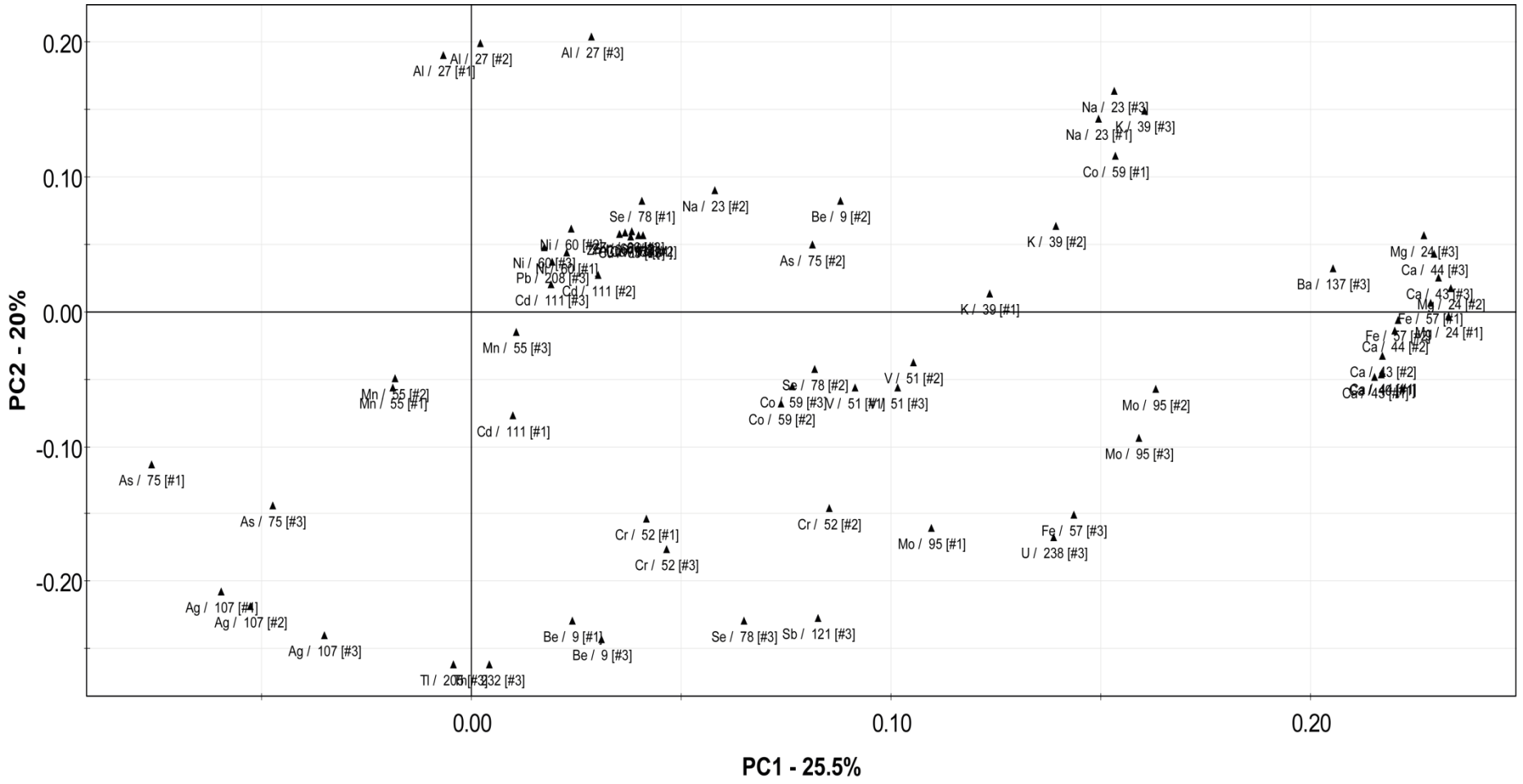


Figure 4-34. PCA loadings plot displaying all trace elements and heavy metals of interest for tap and bottled water. 45.5% of total data variance is again demonstrated by the first two principal components.

Macroelements sodium, calcium, magnesium, potassium and iron are strongly associated with tap water samples, as has been demonstrated throughout the comparison of potable water samples in this section.

Chromium, silver, arsenic, selenium, beryllium, molybdenum, antimony and uranium appear to be associated with the bottled water samples analysed. The known association of antimony with bottled waters was highlighted in section 2.2 of Chapter Two. Antimony-based catalysts account for more than 90% of PET manufacture worldwide. Literature has shown that as a result, antimony leaches into water contained in PET bottles; however, this leaching is not significant enough to cause unsafe levels of antimony to be recorded in the bottled water samples analysed in this research.

Further investigation into the levels of trace elements and heavy metals found in commercial bottled water brands allowed interesting comparisons between the concentrations of vital elements promoted by each brand, and the corresponding concentrations recorded in this research.

4.2.5.2.2 Raw Data and Chemometric Analysis of Bottled Water Brands

The contents of each bottled water sample as determined by ICP-MS analysis and PCA can be compared to what each brand claims to be present or absent from their water. The first bottled water sample (B1) is Aroona Sports Body Quencher, a brand said to be bottled 'at the source' from a valley in the Blue Mountains of New South Wales since 1893 (Aroona Pure Spring Waters, 2013). This brand claims to have concentrations equal to or less than those presented in Table 4-12. The maximum concentrations returned for each of the elements when analysed in this research are compared in Table 4-12.

Table 4-12. Comparison of the maximum concentrations for each element provided by the Aroona brand, and the maximum concentrations from the ICP-MS analysis against Agilent CRMs performed in this research.

Element	Aroona Brand (µg/L)	ICP-MS analysis (µg/L)
Calcium	600	1810
Potassium	800	1980
Magnesium	620	2350
Sodium	2800	8470

The exceedence of concentrations reported by the brand should not be a concern to consumers, as elements such as these are vital to human health, and neither health nor aesthetic guidelines are surpassed when this brand is compared to the 2011 ADWG.

Samples B2, B3, B9 and B11 are also described as 'spring waters': Frantelle Natural Spring Water, Coles Australian Natural Spring Water, Mount Franklin: Australia's Premium Spring Water and Cool Ridge Australian Spring Water respectively. Both the Frantelle and Cool Ridge brands are owned and operated by Schweppes. Coles Natural Spring Water is produced by Mountain H_2O and is said to come from underground springs located at the foothills of the pristine Victorian Alps; it then passes through a four stage micro-filtration system, UV sterilisation and ozonation to maintain the purity of the water (Mountain H2O, 2013). Similarly, Mount Franklin claims its spring water is collected locally and bottled daily, and is filtered three times via micro filters to ensure purity and quality (Mount Franklin, 2012). Results of any water quality analyses performed by these brands are not available to the public.

Two samples, B6 and B10 were sparkling bottled waters: San Pellegrino and Santa Vittoria: Sparkling Italian Mineral Water, respectively. San Pellegrino Sparkling Natural Mineral Water flows from a thermal spring at the foot of a dolomite mountain, on the right side of the Brembana Valley north of Italy (Nestle Waters North America Inc., 2011). A water analysis report for this brand for the first quarter of 2011 tested various inorganic minerals and metals. Those relevant to this research are tabulated in Table 4-13, and are compared to the maximum results achieved through ICP-MS analysis in this work.

Table 4-13. Comparison of the maximum levels of trace elements and heavy metals of interest from a 2011 Water Analysis Report from San Pellegrino (Nestle Waters North America Inc., 2011) against the maximum element concentrations from the ICP-MS analysis performed in 2013 against Agilent CRMs.
ND - not detected.

Element	San Pellegrino Report (µg/L)	ICP-MS analysis (µg/L)
Aluminium	36	0.133
Antimony	2.3	0.719
Arsenic	ND	2.18
Barium	16	17.5
Beryllium	ND	0.155
Cadmium	ND	0.0048
Calcium	170 000	283 000
Chromium	ND	6.12
Copper	ND	2.30
Iron	ND	3045
Lead	ND	1.44
Magnesium	50 000	75 000
Manganese	ND	0.419
Nickel	ND	2.45
Potassium	2600	3540
Selenium	ND	5.46
Silver	ND	1.32
Sodium	33 000	49 300
Thallium	ND	0.721
Zinc	ND	0.0136

Originally the levels of these 'minerals and metals' were measured in milligrams per litre by San Pellegrino, hence the high number of elements that were not detected in the analysis. Again, the concentrations of macroelements calcium, sodium, potassium and magnesium found in this research are greater than the levels reported by this brand, however, this is no cause for concern are there are no health guidelines for these elements. Additionally, the concentrations of copper, arsenic and lead measured for this research are below the health guidelines for these heavy metals according to the 2011 ADWG. Despite all trace element

and heavy metal concentrations in this bottled water brand being below the Australian Drinking Water Guidelines, this sample was considered an outlier when analysed using PCA (see Figure 4-33). This bottled water brand is carbonated, and it was inferred that this may contribute to the significant variance between it and the other bottled water brands analysed.

Santa Vittoria is also bottled in northern Italy and is lightly sparkling, or carbonated. This brand claims to contain an extremely low sodium level (Cantarella Bros, 2012). The level of sodium found in the analysis of this bottled water brand was 1350 µg/L. This is indeed the lowest sodium level of all bottled water brands tested by a margin of 1600 µg/L to the next lowest sodium level in a brand, and over 47 000 µg/L to the brand containing the highest level of sodium.

The low sodium content as advertised by this brand would be of particular importance to consumers on salt restricted diets for medical purposes, such as those with Meniere's disease, kidney or liver disease. This research has demonstrated that Santa Vittoria is indeed the bottled water brand with the lowest sodium content as advertised, and as a result, is the best choice for health conscious consumers.

The remaining bottled water samples B4, B5, B7 and B8 are Nobles Purearu Pure Water, evian® Natural Mineral Water, Pump Pure Water and Cocobella Coconut Water. As previously mentioned, the brand Cocobella, sample B8 was considered an outlier compared to other bottled water samples and tap water samples. Despite being "naturally rich" in elements like potassium, calcium, sodium and magnesium, this hand –harvested coconut water is clearly different from all other brands analysed. Pump is owned by Coca-Cola©, who do not disclose any information regarding the nutrient levels in this water.

Nobles Purearu Pure Water claim that a variety of filters and reverse osmosis ensure that this water is 100% free from chlorides, metals, sodium, fluoride and inorganic minerals like nitrates (Noble Beverages, 2008). The maximum concentrations of sodium, calcium, potassium and magnesium in Nobles Purearu Pure Water as measured during this research are 2950 µg/L, 413 µg/L, 1070 µg/L and 14.8 µg/L respectively.

Even though this bottled water sample was not 100% free of these elements as advertised, it does contain the lowest concentrations of these macroelements when compared to the remaining 10 bottled water brands analysed, with the exception of Santa Vittoria, which had the lowest sodium concentrations of all brands. Additionally, "100% free" is

considered a relative term, because if the water were totally free of these ions, it would be dangerous to consume and would cause loss of minerals from cells in the body.

Finally, evian® Natural Mineral Water, sample B5, originates in the French Alps, slowly acquiring a unique mineral balance and boasting a low sodium content (evian, 2013). The levels of sodium, potassium, calcium and magnesium in this bottled water brand are provided by evian® and compared with the concentrations found in this research in Table 4-14.

Table 4-14. Comparison of the maximum concentrations for each element provided by evian® and maximum element concentrations from the ICP-MS analysis performed against Agilent CRMs in this research.

Element	evian® Brand (µg/L)	ICP-MS analysis (µg/L)
Sodium	6500	11 200
Potassium	1000	1800
Calcium	80 000	159 000
Magnesium	26 000	46 100

As seen in Table 4-14, higher concentrations of these elements were measured in this research, however, there are no health guidelines for sodium, potassium, calcium and magnesium, and such small amounts of these macroelements are required for good health. evian® has the second greatest concentration of calcium of all brands tested, where San Pellegrino has approximately double the calcium concentration found in evian®.

Beyond these raw data comparisons, the chemometric technique Hierarchical Cluster Analysis (HCA) was used to elucidate the similarities and differences between all of these bottled water brands.

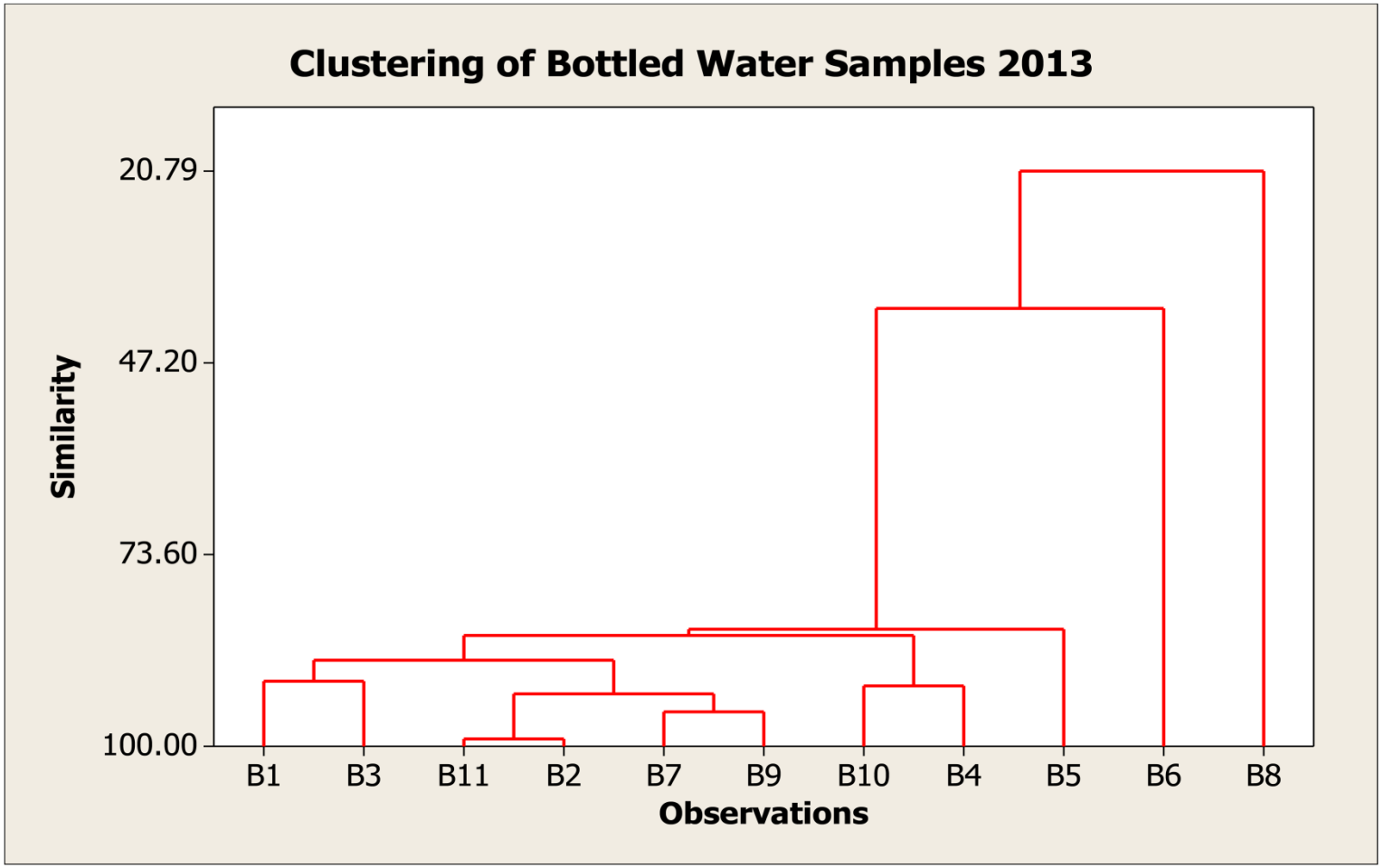


Figure 4-35. HCA dendrogram showing the similarity between bottled water brands tested in 2013. Squared Euclidean Distance metric and Average Linkage were used for the clustering of this data according to trace elements and heavy metals analysed.

The resulting dendrogram, shown in Figure 4-35, confirms the results achieved with PCA, whereby samples B6 and B8, San Pellegrino and Cocobella Coconut Water, are seen to be the most dissimilar samples to all other brands. Next, it can be inferred that samples B10 and B4, Santa Vittoria and Nobles Pureau Pure Water, are clustered because these brands possessed some of the lowest concentrations of macroelements, particularly sodium and potassium, of all other brands.

Finally, the large cluster of samples B1, B3, B11, B2, B7 and B9 are the remaining brands that class themselves as 'spring waters'. Sample B5, evian®, is also a 'spring water', but is more separate from the remaining spring waters. This is believed to be because this brand originates from France and promotes a balance of minerals in the water, in contrast to spring water brands who market the absence of minerals from the water.

Overall, it can be seen from direct comparisons of element concentrations, PCA and HCA, that all bottled water brands tested are reasonably similar to each other. The levels of macroelements present in these samples can be considered low, and therefore contribute very little to the recommended daily intake of such minerals. As a result, consumers have no cause for concern regarding the levels of trace elements and heavy metals present in bottled water.

4.2.5.3 Chemometric Analysis of Raw Water Sources

In addition to potable waters collected for analysis, another important aspect of this research was the collection and analysis of raw water samples collected from dams, lakes, rivers and creeks, as well as two treated water samples from Mt Crosby West Bank WTP.

The pH and hardness of each raw water source was determined and is displayed in Table 6-7 of Appendix C-3. In general, the pH of the various raw water sources analysed ranged from 5.6 to 8. The highest pH values, pH 8.01 and 7.99, were recorded for the treated water samples taken from reservoirs one and two respectively on Camerons Hill. Hardness was calculated by totalling the concentrations of calcium and magnesium ions present in the raw water samples. The minimum hardness was associated with Ewan Maddock Dam on the Sunshine Coast and was 4105 µg/L, while the maximum hardness of 260 400 µg/L was recorded for Oxley Creek.

As shown previously in Figure 4-25, raw water is easily distinguished from other potable water sources. Similar to tap water in Figure 4-26 and Figure 4-27, the raw water samples collected can be distinguished based on location. Analysing the treated and raw water samples separate from any other water types will give insight into the influence of trace elements and heavy metals on these water sources.

Mercury and iron 56 were removed from this analysis, and cadmium (^{111}Cd) was also removed by SIMCA-P 10.0 for possessing little to no variance. Additionally, the sample from Oxley Creek was previously shown to be an outlier, and so was excluded from this analysis.

The distinction of raw water sources can be seen with PCA and HCA. Additionally, PROMETHEE and GAIA offer insight into which raw water source is the most preferred water source in South East Queensland.

Figure 4-36, the PCA scores plot, demonstrates the relationships between these raw and treated water samples. The PCA scores plot for raw and treated water samples represents a significant amount (67.8%) of data variance, and shows all samples within the Hotelling T2 95% confidence ellipse. The corresponding sample names and collection locations can be referenced against Table 6-4 in Appendix C-2.

The Oxley Creek (OC) sample was originally included and fell outside of the Hotelling T2 95% confidence ellipse. It was therefore considered an outlier and excluded from further analysis. Oxley Creek is one of the main tributaries to the Brisbane River. The health of this creek has long been in question, and scores an F (the lowest grade assigned) on the Health-E Waterways report card for 2012 (The University of Queensland, 2012). The turbidity, effects of sand mining and the sample site location downstream of the Queensland Urban Utilities Oxley Sewage Treatment Plant all contribute to the environmental concerns surrounding Oxley Creek.

There is little clustering observed in Figure 4-36. This result is not unexpected due to the large geographical distance between these sample sites as well as the difference in sample sites, i.e. sand vs. soil, as described in Table 6-4 in Appendix C-2. However, the Sunshine Coast samples from Baroon Pocket (BP) and duplicate samples from Ewan Maddock Dam (EM and EM2) are loosely clustered.

Additionally, the treated water samples, CH1 and CH2, and raw water samples MCR and CC (Mt Crosby Raw and College's Crossing respectively) are clearly clustered on the left-hand side of the PCA scores plot. These samples are strongly related because the MCR raw water sample and the two treated water samples from the Cameron's Hill Reservoirs (CH1 and CH2) were all collected from the Mt Crosby West Bank WTP, while College's Crossing is located four and a half kilometres downstream from the Mt Crosby WTP.

These PCA results are confirmed by Figure 4-37, the HCA dendrogram for these samples. The Squared Euclidean Distance metric and the Average Linkage algorithm were applied to this data, thereby remaining consistent with the method applied to the historical batch by batch data.

Euclidean distance is a standard mathematical measure of distance, and is the square root of the sum of squared differences; therefore, Squared Euclidean Distance method uses the square of the Euclidean method. Average linkage means that a more central measure of location is used through the determination of the mean distance between one observation in one cluster and an observation in another cluster. All data was auto-scaled for HCA in Minitab 16 Statistical Software (Minitab Inc., 2010).

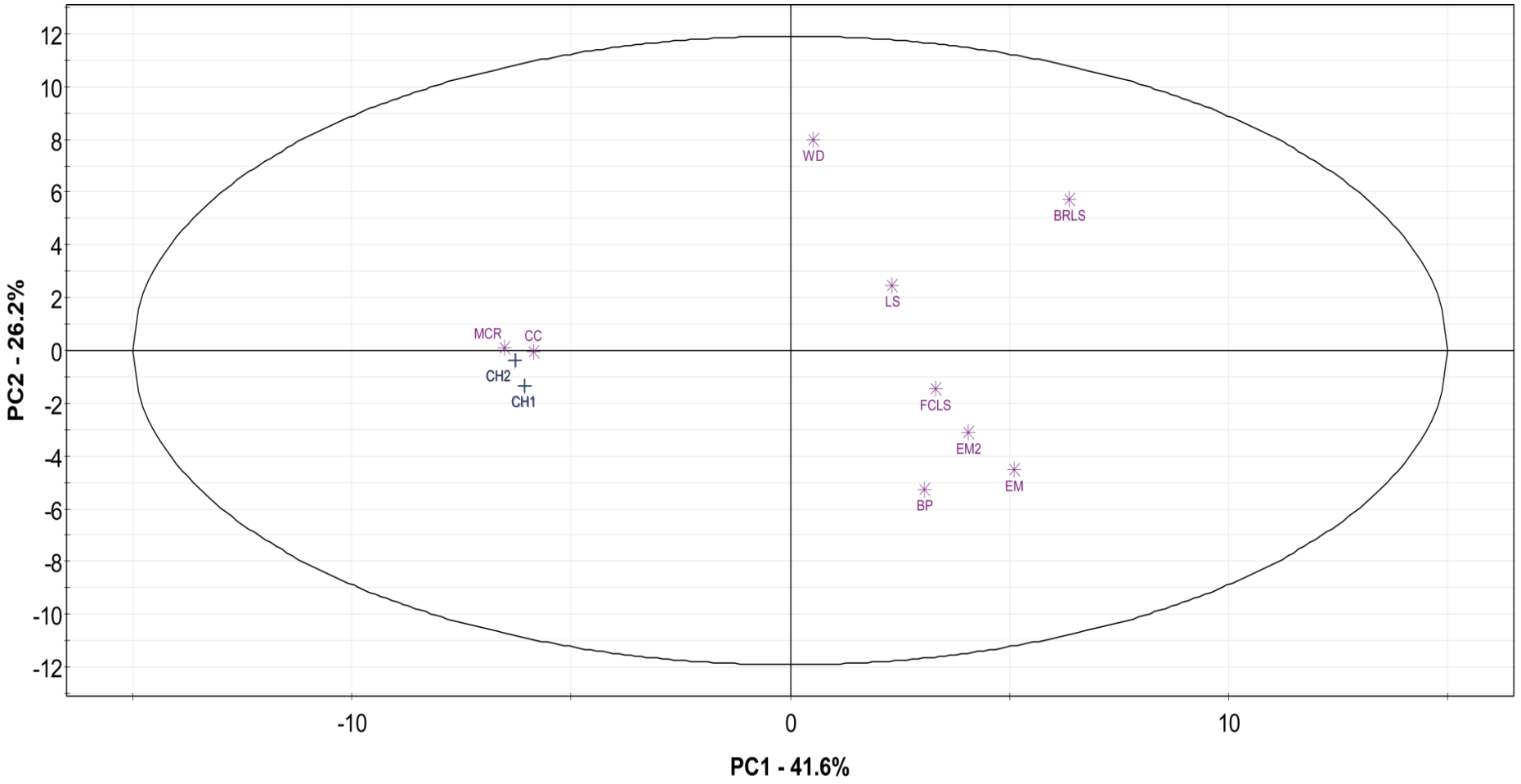


Figure 4-36. PCA scores plot displaying the raw water sources. 67.8% of total data variance is shown. The anomalous Oxley Creek sample was removed from the analysis. The two treated water samples are represented by the blue-grey crosses, and the raw water samples by the purple stars.

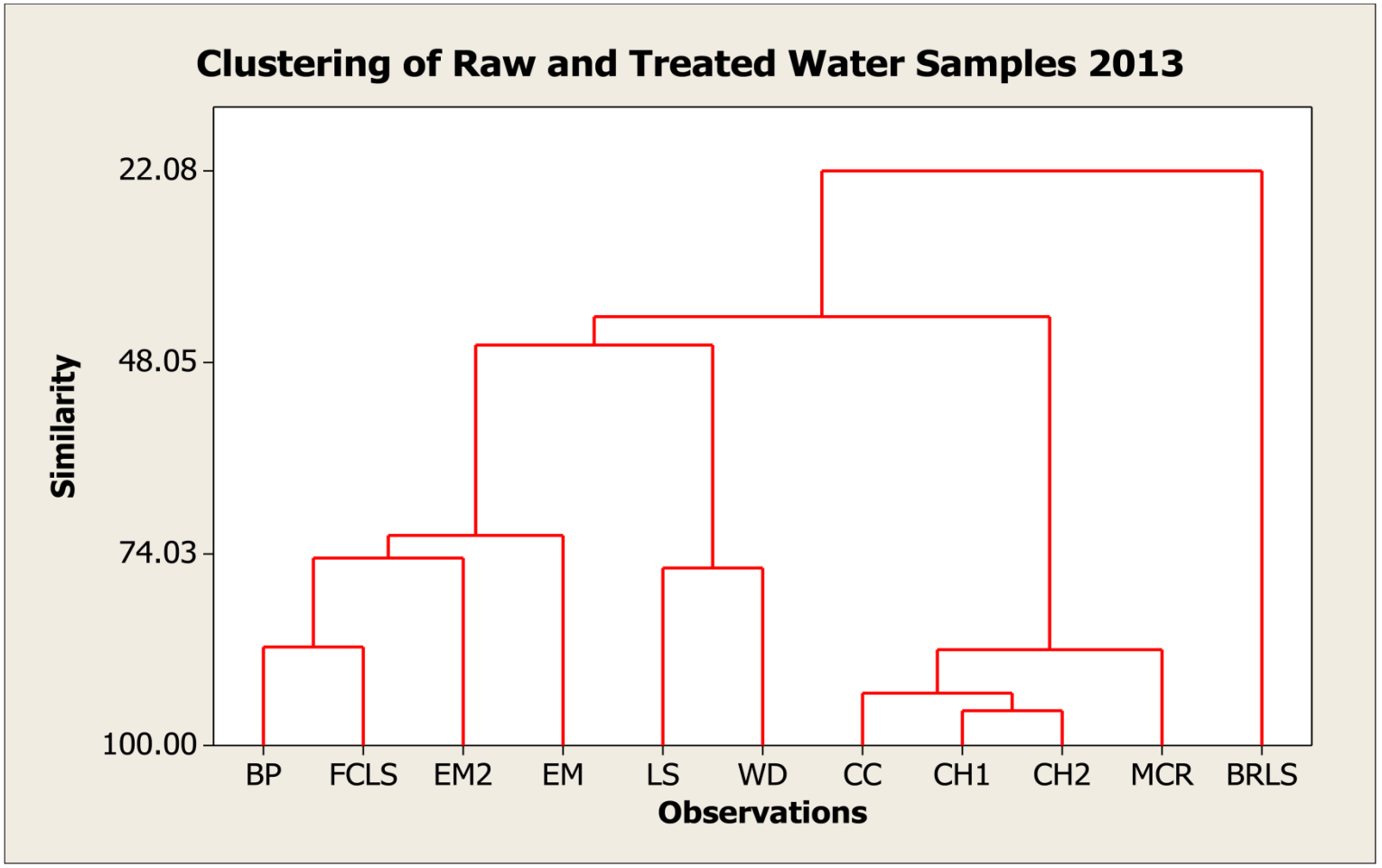


Figure 4-37. HCA dendrogram displaying the similarity between all treated and raw water samples analysed. The Oxley Creek (OC) sample has been excluded.

Clustering of like samples, observed previously in Figure 4-36, is seen again in Figure 4-37. The Oxley Creek (OC) sample was clearly the most dissimilar from all other samples, and as a result, it was removed from this cluster analysis. Most similar are the treated water samples from Cameron's Hill Reservoir, CH1 and CH2, which are clustered with the raw water samples taken from very similar locations at Mt Crosby and College's Crossing.

Next, the samples from Lake Somerset (LS) and Wivenhoe Dam (WD) are clustered together. Somerset and Wivenhoe Dams are geographically close and water from Somerset Dam is often released into Wivenhoe Dam to supplement the natural flow of the Brisbane River. Therefore, it is logical that these two samples are closely related.

The duplicate samples from Ewan Maddock Dam on the Sunshine Coast form another cluster together with BP and FCLS, the sample from Baroon Pocket Dam at the Sunshine Coast and Forgan Cove at Lake Samsonvale. The inclusion of FCLS in this cluster is unexpected, given the geographical distance between it and the other two dams.

Additionally, the significant distance seen between samples BRLS and FCLS in both Figure 4-36 and Figure 4-37 is unexpected, as these samples were both collected from two locations at Lake Samsonvale, one from Bullocky Rest and the other from Forgan Cove.

The analysis of the PCA loadings plot for these treated and raw water samples may therefore add insight into the reasons for the observed clustering of samples.

The cluster of samples collected from Mt Crosby and College's Crossing is the only cluster on the left-hand side of the scores plot in Figure 4-36 and so appears to be most strongly associated with calcium, sodium, magnesium, molybdenum, nickel, iron, copper and uranium in Figure 4-38.

The samples from the Sunshine Coast, Baroon Pocket (BP) and Ewan Maddock (EM) Dams, as well as a sample from Lake Samsonvale (North Pine Dam) taken from Forgan Cove (FCLS) are shown in the negative quandrant of the right-hand side of the scores plot. So, based on Figure 4-38, these samples are most significantly associated with zinc.

The remaining samples from Lake Somerset, Wivenhoe Dam and another from Lake Samsonvale taken from Bullocky Rest are shown in the positive quadrant on the right-hand side of the Figure 4-38, and are therefore associated with selenium, silver, manganese, cobalt, chromium, lead and aluminium.

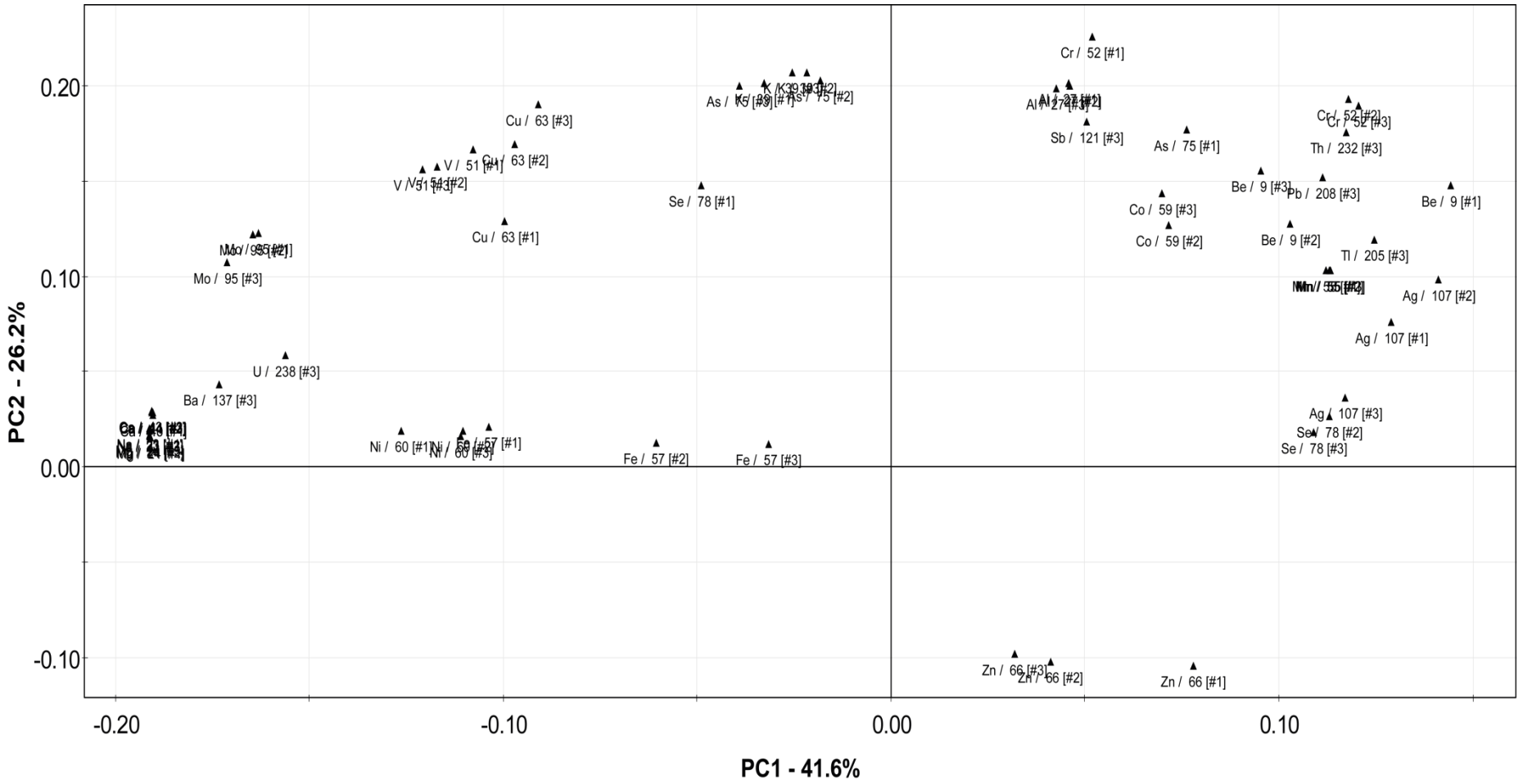


Figure 4-38. PCA loadings plot for raw water sources displaying all trace elements and heavy metals analysed, corresponding to the scores plot of Figure 4-36. 67.8% of the data variance is displayed.

To supplement the observations made in regard to the trace elements and heavy metals associated with the raw water sources from Figure 4-36 and Figure 4-38, sediment data from the Geological Survey of Queensland supplied by the state government Department of Natural Resources and Mines (DNRM) were examined.

4.2.5.3.1 Comparison to Sediment Concentrations

Throughout this research it has been shown that metals are ubiquitous in the environment. Sediments are defined as loose sand, clay, silt and other soil particles that settle at the bottom of a body of water (MARC, 2014). They play an important role in elemental cycling in the aquatic environment, and are responsible for transporting a significant portion of many nutrients and contaminants (WHO, 1996).

In the environment, metal species can exist as freely dissolved metal, or as organic and inorganic metal complexes. These metal species may consist of trace elements and heavy metals released into waters and sediments as a result of weathering and diagenesis, or as the result of anthropogenic activities (US EPA, 2007).

The availability of these metals is mediated by sediment-water exchange processes that can result in the release or remobilisation of chemicals from the sediment bed (US EPA, 2007). Interestingly, sediments can hold up to a million times more metal than an equivalent volume of water. For humans, the route of ingestion of metals from sediments is through water used for drinking, swimming and other water-based recreational activities (US EPA, 2007). Therefore, it is important to consider the relationship between sediments and water quality of raw water sources in this research.

The areas investigated in a report by DNRM entitled: Queensland Mineral Prospectivity Atlas, that cross over with the areas from which raw water samples were collected include that of the Mary River, and two sites from different points in the Brisbane River. The geochemistry presented in this report reflects the average composition of sediments within the catchment and is therefore useful to establish the background elemental concentrations of sediment.

In 1988, Baroon Pocket Dam was constructed on Obi Obi Creek. Obi Obi Creek originates from Mary River (TS1085), a large river on the Sunshine Coast. Similarly, sediment data were taken from two points on the Brisbane River, one (TS1133) from College's Crossing, and one (TS1127) from almost directly in between Lake Somerset and Lake Wivenhoe. Sampling sites are shown in Figure 6-33 in Appendix C-3.

The raw water sources sampled from the Sunshine Coast area, particularly Baroon Pocket Dam, were associated with zinc according to Figure 4-38. According to the Queensland Mineral Prospectivity Atlas, concentrations of 30 000 to 37 500 mg/kg of iron were found in the sediments of the Mary River sampling site (TS1085), as well as 48 to 67 mg/kg of zinc. The concentrations of these elements appear to be average when related to concentrations detected at the other sites depicted in Figure 6-33. There are also higher levels of silver, 0.025 – 0.05 mg/kg, in these sediments compared to the two other sites of interest in the Brisbane River (Tang & Brown, 2011).

Figure 4-38 shows that the raw water samples collected from Mt Crosby West Bank WTP and College's Crossing are related to macroelements calcium, sodium, magnesium and iron, as well as molybdenum, nickel and copper. The sediment concentrations of these elements at the corresponding site TS1133 on Figure 6-33 are average in comparison to Brisbane River site TS1127 and Mary River site TS1085; however, this site (TS1133) reported the highest concentration of magnesium, 8200 mg/kg, in sediment at all sites tested.

Finally, Figure 4-38 indicates that samples collected from Lake Somerset, Wivenhoe Dam and another from Lake Samsonvale taken from Bullocky Rest are associated with selenium, silver, manganese, cobalt, chromium, lead and aluminium. Again, the concentrations of these trace elements and heavy metals in the sediments at site TS1127 are average in comparison to concentrations found at the other Brisbane River and Mary River sites, TS1133 and TS1085, with the exception of lead. Concentrations of lead in sediments at site TS1127 are the highest, ranging from 6 to 10.5 mg/kg (Tang & Brown, 2011).

There are many different reactions and rates associated with the release of trace elements and heavy metals from sediments into water. The external information provided by the Queensland Minerals Prospectivity Atlas provides an interesting, qualitative indication of the abundance of trace elements and heavy metals in the catchment areas around South East Queensland. Next, the preferential ranking of the raw water sources based on water quality can be achieved through the use of PROMETHEE and GAIA.

4.2.5.4 PROMETHEE and GAIA Analysis of Raw Water Sources

The use of qualitative ranking techniques, PROMETHEE and GAIA can be applied for a comprehensive analysis of the raw water samples. A PROMETHEE rank order based on the trace element and heavy metal concentrations in each sample will determine which raw water source is most preferred to all others prior to the treatment and mixing of raw water sources at treatment plants for bulk supply. Similarly, a GAIA plot of this same data will complement the results achieved by PCA.

The water bodies analysed in this research were used as a source of raw water and for recreation activities by the general public. It was therefore determined that these ecosystems could be classified as slightly-moderately disturbed. Following the recommendation for the protection of different ecosystem conditions explained in the Australia and New Zealand Environment Conservation Council/Agricultural and Resource Management Council of Australia and New Zealand (ANZECC/ARMCANZ, 2000) water quality guidelines for toxicants, the 95% protection level trigger values for freshwater were applied.

Initial comparisons of the raw water sample data and the ANZECC/ARMCANZ (2000) water quality guidelines for toxicants revealed that almost all of the raw water samples analysed in this research conform to the 95% protection level trigger values. Mercury and iron 56 were removed from this analysis due to unreliable results, as discussed in section 4.2.4.1. The heavy metals that exceed these guideline trigger values in each raw water source are displayed in Table 6-7 of Appendix C-3. Oxley Creek reported alarming concentrations of arsenic, chromium (as Cr(VI)), copper and silver well in excess of the guideline trigger values. Both treated water samples (CH1 and CH2), both samples from Lake Samsonvale (BRLS and FCLS), and the samples collected from Lake Somerset, Wivenhoe Dam and Ewan Maddock Dam all contained levels of aluminium greater than the guideline trigger value of 55 µg/L. Additionally, the raw water samples from Mt Crosby, Lake Somerset and Wivenhoe Dam all exceeded the 1.4 µg/L trigger value for copper. Finally, all raw water sources analysed exceeded the trigger value for silver by more than 1 µg/L.

PROMETHEE and GAIA were subsequently performed on raw water sources, and the concentrations of all trace elements and heavy metals in these samples were compared to the ANZECC/ARMCANZ (2000) water quality guidelines for toxicants, not the 2011 Australian Drinking Water Guidelines (ADWG), as these are not potable waters.

The objects, or raw water sources, are referred to as actions, and elements and tuning steps are known as the criterion. The ranking of actions was facilitated by pair-wise comparisons of the criterion of each action against the ANZECC/ARMCANZ (2000) water quality guidelines for toxicants. For these comparisons, the V-shape preference function was chosen, because previous research, discussed in section 3.7.6 of Chapter Three, demonstrated that this preference function has been widely applied to environmental work, and offers the best outcome.

Additionally, the minimum (rather than maximum) variable modelling option was selected for the concentrations of trace elements and heavy metals in a sample. The minimum value is preferred for the criterion due to the reasonable assumption that the raw water sources (actions) with minimal trace element and heavy metal contamination would be the most preferred.

The ranking results are represented by preference flow values. Phi + (Φ+) is the positive flow which measures how much an action is preferred over other actions. The negative flow, phi - (Φ-), measures how much other actions are preferred over an action. The balance between these positive and negative preference flows is phi (Φ), the net flow, where the strength (Φ+) and weakness (Φ-) of the action is taken as a single value. As a result, Φ can be positive or negative, where the larger (positive) Φ value represents the better action.

Firstly, the GAIA plot for all raw water samples contains the actions, or raw water sources, and the criterion, the trace elements and heavy metals, on the same plot. Plotting the actions and criterion on the dimensionless axes of the GAIA plane reveals extra information that can be used to make decisions regarding the most preferred action, and the most influential criteria in that decision.

GAIA employs the PCA method of reducing the dimensionality of the data whilst minimising the loss of information. There is also a pi (π) decision axis that points in the direction of the best decision and represents the weighting of the criteria (Mareschal, 2012). A long decision axis is more reliable. The raw water sources, trace elements and heavy metals that are in line with the pi decision axis are favourable in the decision. All sampling codes for raw water sources and collection location descriptions can be referenced against Table 6-4 in Appendix C-2.

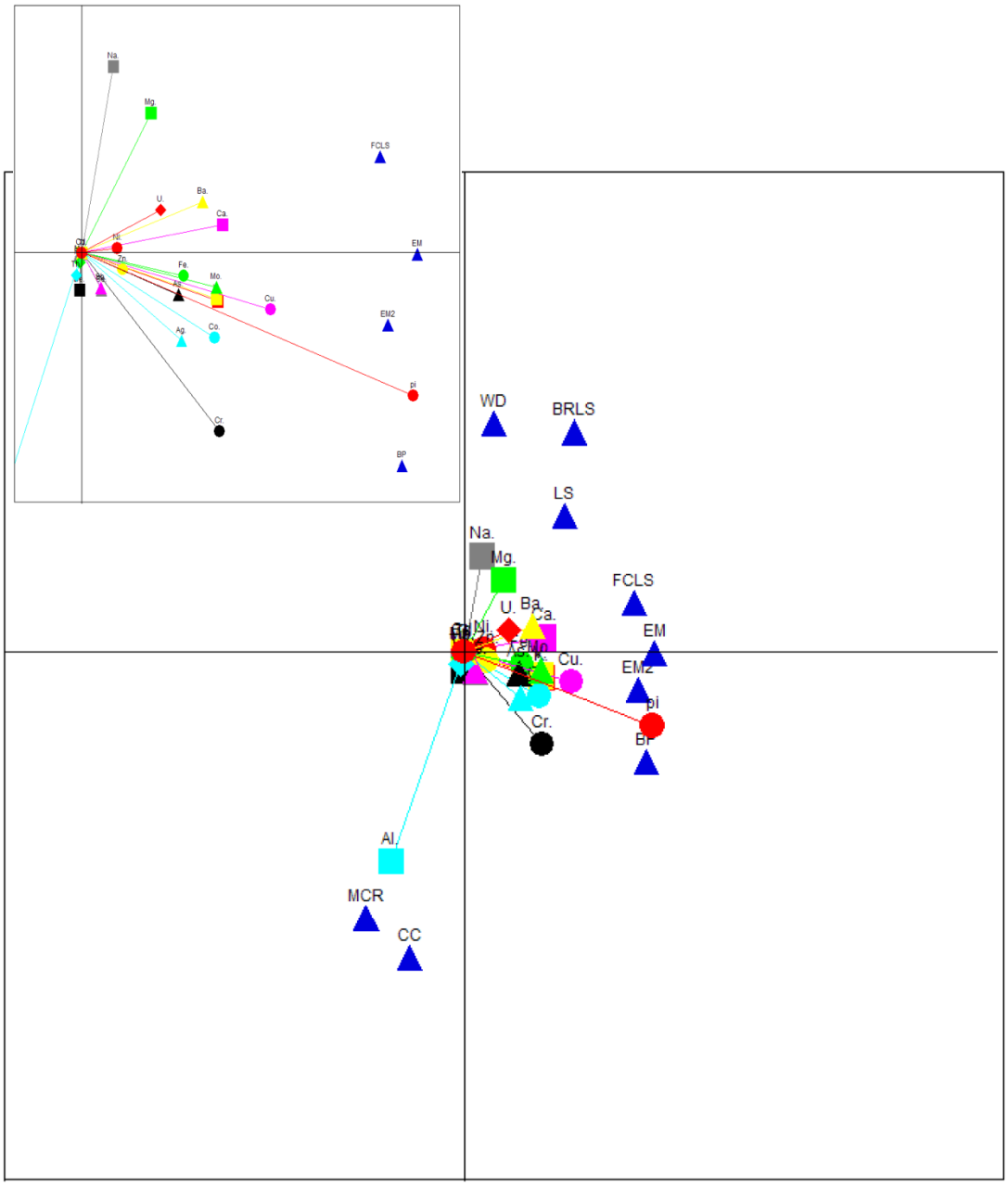


Figure 4-39. GAIA plot displaying all objects (dark blue triangles) and variables (coloured shapes) from the analysis of raw water sources compared to the ANZECC/ARMCANZ (2000) water quality guidelines for toxicants. The pi decision axis (red circle) is also pictured. The main GAIA plot is displayed at 205% magnification, and inset at 800% magnification.

The Oxley Creek sample is not visible in Figure 4-39 as it is situated on the far left hand side of the GAIA plot, in the opposite direction of the pi decision axis. This result it similar to Figure 4-36, the PCA scores plot, and Figure 4-37, the HCA dendrogram, therefore, it can be definitively stated that the Oxley Creek (OC) sample is an outlier and is the least preferred

of all the raw water samples analysed in this research. All other samples are significantly closer to the decision axis. The most preferred raw water sources based on this GAIA plot are those from the Sunshine Coast, Baroon Pocket and Ewan Maddock Dams.

The variables shown on this GAIA plot are grouped, that is, the data from tuning steps [#1] to [#3] for each element is combined and represented as one variable data point. A magnified view of the centre of the GAIA plane (inset) in Figure 4-39 provides information on the importance of the elements of interest.

The length and orientation of these axes is important. Elements sodium and magnesium express similar information about the objects due to the length and close proximity of these axes. Alternatively, aluminium and magnesium represent contrasting information because their axes point in opposite directions. Copper, potassium, vanadium, molybdenum and cobalt can be described as the most important criteria for the preferential rank order of the raw water sources as the axes of these elements have satisfactory length and the closest proximity to the pi decision axis.

When the relationships between the raw water sources and trace elements and heavy metals in Figure 4-39 are examined, aluminium appears to have the greatest influence on the raw Mt Crosby and College's Crossing samples. Concentrations of potassium, vanadium, molybdenum, copper, calcium, iron, cobalt and barium are associated with the Baroon Pocket, Ewan Maddock and Lake Samonsonvale Forgan Cove samples, while sodium and magnesium have the most direct influence on the Lake Samsonvale Bullocky Rest, Lake Somerset and Wivenhoe Dam samples. The remaining trace elements and heavy metals analysed extend a short distance from the origin of the GAIA plot, indicating that they have little variance and therefore little effect on the raw water samples.

The results from the GAIA plot differ slightly to those inferred from the PCA loadings plot. PCA is an exploratory pattern recognition technique that demonstrates the relationships between the objects (scores plot) and the relationships between variables (loadings plot). Whereas GAIA demonstrates the relationships between the objects and variables, in comparison to a set of guidelines, as well as assisting the decision maker by indicating the best decision based on all of the data. GAIA is considered a form of PCA, and PROMETHEE serves as the pre-treatment method for the data plotted, and no other pre-treatment is required.

The raw water samples were preferentially ranked in comparison to the ANZECC/ARMCANZ (2000) water quality guidelines for toxicants. PROMETHEE results can be displayed as a partial ranking of samples, or a complete ranking of samples. PROMETHEE I Partial Ranking does not force samples into a rank order, but has the option to display a sample as incomparable to another, or on the same level as other samples because it takes into account both the Φ+ and Φ- values.

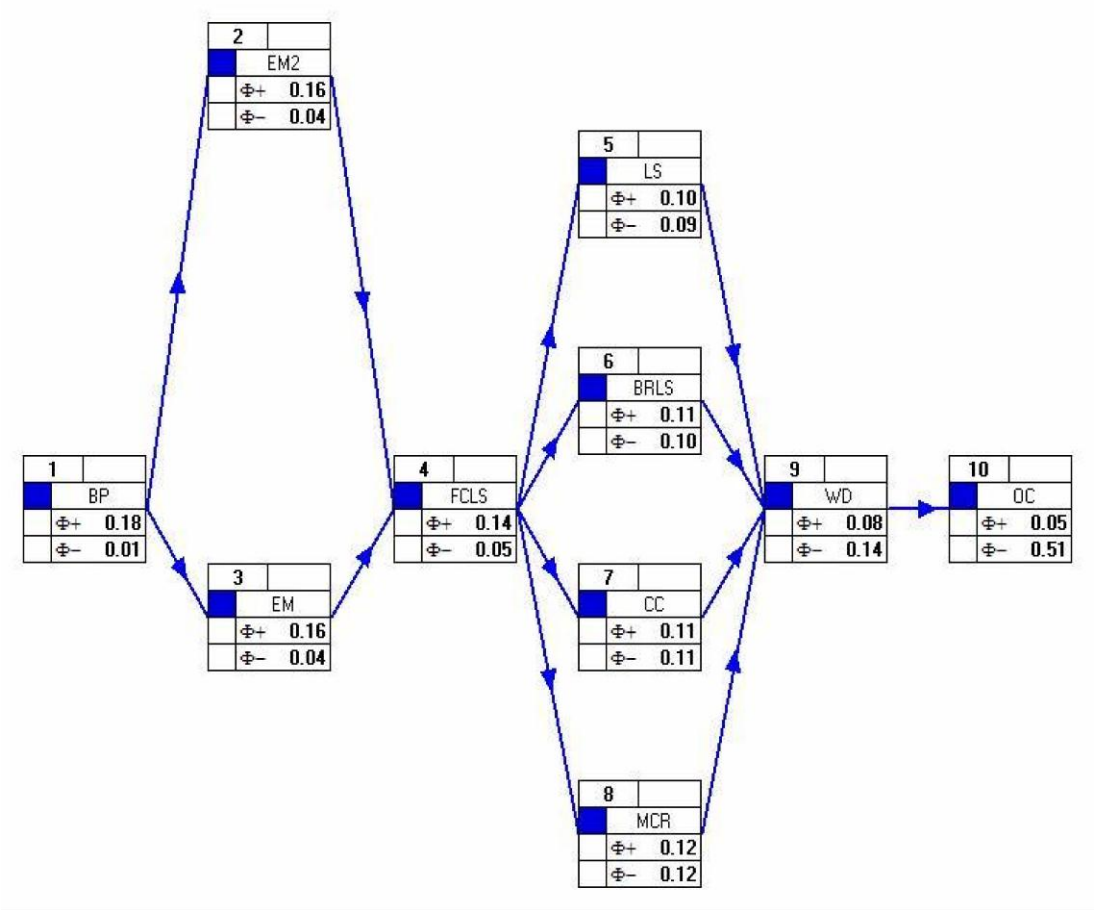


Figure 4-40. PROMETHEE I Partial Ranking of raw water samples based on Φ+ and Φ- values.

Based on the partial ranking of samples, Figure 4-40 explains that the sample from Baroon Pocket Dam (BP) is most preferred, followed by the duplicate Ewan Maddock Dam (EM and EM2) samples, which both possess the same Φ+ and Φ- values. Next is Forgan Cove at Lake Samsonvale (FCLS), then the samples from College's Crossing (CC), Mt Crosby (MCR), Lake Somerset (LS) and Bullocky Rest at Lake Samsonvale (BRLS), all of which are incomparable to each other. The sample from Wivenhoe Dam (WD) is next, and finally the Oxley Creek (OC) sample is the least preferred raw water source.

In contrast, PROMETHEE II Complete Ranking orders samples based solely on their net Φ value, as seen in Figure 4-41.

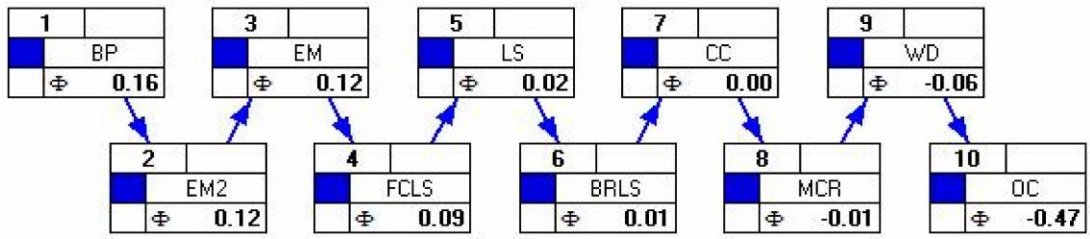


Figure 4-41. PROMETHEE II Complete Ranking of raw water samples based on the net Φ value.

The Φ+, Φ- and Φ values for each sample that were used to construct both rankings in Figure 4-40 and Figure 4-41 are summarised in Table 4-15.

Table 4-15. Preference Flow table showing raw water sources in order from best to worst based on all Φ+, Φ- and net Φ values.

Raw Water Source	Source Code	Φ+	Φ–	Φ
Baroon Pocket	BP	0.1772	0.0126	0.1646
Ewan Maddock Dam 2	EM2	0.1588	0.0366	0.1222
Ewan Maddock Dam	EM	0.1609	0.0413	0.1196
Forgan Cove Lake Samsonvale	FCLS	0.1415	0.0466	0.0949
Lake Somerset	LS	0.1045	0.0865	0.0181
Bullocky Rest Lake Samsonvale	BRLS	0.1133	0.1020	0.0113
Colleges Crossing	CC	0.1148	0.1113	0.0035
Mt Crosby Raw	MCR	0.1155	0.1250	-0.0095
Wivenhoe Dam	WD	0.0777	0.1373	-0.0596
Oxley Creek	OC	0.0494	0.5145	-0.4650

The values listed in Table 4-15 show that Baroon Pocket and Oxley Creek are by far the most preferred and least preferred raw water sources sampled in South East Queensland, when compared against the ANZECC/ARMCANZ (2000) water quality guidelines for toxicants. Baroon Pocket Dam is one of the 12 key water supply dams in the SEQ region, as highlighted in Table 1-1 of Chapter One, and is part of the water grid that supplies the greater Brisbane area (Figure 4-28).

Despite the minor exceedences of several heavy metals across the raw water samples analysed, and with the exception of Oxley Creek, overall it can be concluded that the dams, lakes and rivers from which raw water is sourced for treatment and delivery within South East Queensland can be deemed healthy.

4.2.5.4.1 Summary of Findings

All chemometric techniques applied to the data so far have assisted in fulfilling several objectives and answering the first question proposed for this research. Sections 4.2.5.1 to 4.2.5.4 of this chapter have determined that heavy metal fingerprints of various water sources can be distinguished.

Firstly, it was shown that raw water is easily distinguishable from treated, potable water through the comparison of tap water, treated water and raw water samples analysed using PCA. Next, by investigating the concentrations of trace elements and heavy metals present in treated water from Mt Crosby West Bank WTP, in the mains water distribution system, and then at household taps, it was discovered that the concentrations of the trace elements and heavy metals analysed do indeed change from leaving the WTP to reaching consumers' taps.

It was also shown that trace element and heavy metal concentrations can be used to distinguish waters by area, as evidenced by examining tap water independently, and observing clustering based on sample site. Additionally, it was concluded that the original raw water source could not be determined from analysis of potable water samples, due to the rigorous treatment processes applied and the mixing of water sources within the SEQ water grid.

Finally, performing PCA on tap, tank, filtered and bottled waters showed that different potable water sources can be distinguished from one another. Similarly, the use of PROMETHEE and GAIA in addition to PCA and HCA techniques demonstrated that raw water sources are also distinguishable based on their trace element and heavy metal concentrations, and that particular raw water sources are preferred over others.

Another research question (Question II.) asked if changing climatic conditions affect potable water quality. Using PROMETHEE and GAIA, the year with the best overall water quality in South East Queensland, compliant with the 2011 ADWG, can be determined along with the answer to Question II.

4.2.5.5 Temporal Variations of Data and Changing Climatic Conditions: 2008 to 2013

South East Queensland has experienced tumultuous weather in the past decade. Below average rainfall in 2008 and 2009 did little to relieve the almost decade long drought experienced throughout the state. Then, 2010 was Queensland's wettest year on record, a year that lead into one of the most devastating floods experienced by the state in January 2011. Flood events were also observed in January and March of 2012, then, in contrast, severe fire weather was battled in October.

Following a warm and hot December, January 2013 saw destructive floods, before the year finished with record heat and lowest rainfall since 1938. The occurrence of climatic extremes, like the wettest year on record definitively ending a decade-long drought for the state, and consecutive years of damaging floods, are known to affect water quality.

Most recently, widespread flooding in South East Queensland raised concerns that excess trace elements and heavy metals, among other contaminants, were being washed into water ways from both lithogenic and anthropogenic sources previously untouched by normal water levels. Therefore, it may be inferred that the various weather events experienced by South East Queensland in the past six years have influenced the quality of water supplied to the greater Brisbane area.

The ranking of each year from 2008 to 2013, by the pairwise comparison of mean trace element and heavy metal concentrations against the 2011 ADWG, was facilitated by the chemometric techniques, PROMETHEE and GAIA. The resulting ranking of years was then examined in conjunction with the weather conditions experienced by the region from 2008 to 2013. The following section describes the weather of South East Queensland during this time period, according to the Australian Bureau of Meteorology.

4.2.5.5.1 Weather in South East Queensland: 2008 to 2013

The changing climatic conditions experienced throughout the state, particularly in South East Queensland, may have influenced the quality of drinking water supplied to residents of the greater Brisbane area. It is therefore important to examine the weather conditions from 2008 to 2013, the time period in which yearly analyses of water quality were performed and studied in this research.

2008

Dry, drought conditions were experienced by the state since 2001, and prevailed until January 2007. In 2008, average to below average rainfall seen in 2007 persisted in the south east districts of Queensland, whereas above average rainfall was experienced in central and northern Queensland. In June and July, unseasonal rainfall was above average, and in November, a barrage of severe thunderstorms caused severe damage in south east Queensland, before below average rainfall returned in December. Additionally, average to below average temperatures were recorded for most of the state (Burearu of Meteorology, 2009).

2009

In 2009, below to very much below average rainfall occurred over the south east quarter of the state, excluding the coastal region, which received average rainfall throughout the year. In particular, south east Queensland saw above average rainfall for April and May. The winter of this year was Queensland's hottest and third driest on record, and was associated with a series of dust storms across south east Queensland in September and October. These months, in addition to November, also had below average rainfall (Burearu of Meteorology, 2010).

2010

The year 2010 was Queensland's wettest year on record. Following a dry and hot January, and a wetter than average February, the first few days of March included Queensland's wettest day on record, and induced widespread major flooding of the southern inland area of the state. The state then experienced its wettest September on record. October and November were also very wet months. This weather continued into the state's wettest December on record, where widespread heavy rainfalls enhanced existing or triggered new flooding in many river systems. Additionally, severe thunderstorms affected south east Queensland mid-December, causing one of the most significant floods in Queensland's history (Burearu of Meteorology, 2011).

2011

Continuing from 2010, very much above average rainfall was experienced in January of 2011. In the second week of January, severe flooding, including river and flash flooding, occurred in Brisbane and surrounding areas of south east Queensland, including Toowoomba and the Lockyer Valley. While levels reached by floodwaters in 2010-2011 were not as high as Brisbane's worst flood in 1974, the damage caused by this event was devastating. Over 75% of the state was declared a disaster zone, with much of central and southern Queensland, including Rockhampton, Emerald, Bundaberg, Dalby, Toowoomba, Dalby and Ipswich affected (Hurst, 2011). There were 35 confirmed deaths, and the damage bill was $2.38 billion (Carbone & Hanson, 2012; Uren, 2011). Later in the year, the wettest autumn since 1990 was experienced and included the wettest March on record. Average to below average rainfall was seen from September through to December (Burearu of Meteorology, 2012). Overall, it was a cool year, with several sites setting records for low temperatures.

2012

In 2012, yearly rainfall for south east Queensland was average to below average. However, from January 23 to 27, persistent heavy rain triggered extensive flooding, which continued into February with more rain across the southern inland and westward-flowing floodwaters progressing across southern Queensland. Heavy rain and flash flooding was again experienced on March 23, damaging more than 800 homes in the south east region. In contrast, severe fire weather was experienced in late October, when there were over 60 fires burning throughout the state, and associated smoke could be seen across the state for many months. Severe thunderstorms from November 17 to 18 caused more widespread damage, and some flash flooding occurred around Brisbane. Finally, dry and hot weather in December saw the lowest average rainfall since 2002 (Burearu of Meteorology, 2013a).

2013

Following a warm and dry December, 2013 saw Queensland's average maximum temperature become the highest on record, with a record hot start to the year. However, most of the east coast of Queensland experienced very heavy rainfall from January 22 to 29 as a result of former Tropical Cyclone Oswald. This rainfall resulted in severe flooding in many areas within 200 km of the east coast (Burearu of Meteorology, 2013b). The Rockhampton and Bundaberg regions were particularly affected. In Bundaberg alone, about 2000 homes and 200 businesses were inundated, 1000 homes became uninhabitable, and more than 7500 people were evacuated from the area, making this the

largest evacuation in Australia's history (Paull, 2013). There were six fatalities, and another $2.4 billion worth of damage caused just two years after the devastating flood of January 2011 (Dayton, 2013; Jabour, 2013).

The Flood Impacts Report by SEQ Catchments Ltd (2013) explains how the January 2013 flood varied from the flood of January 2011. Flooding in Brisbane and Ipswich was significantly less than in January 2011; but in the flood of 2013, many regional and suburban streams received considerably higher flows than in January 2011, resulting in significant bank erosion, damage to road and crossing infrastructure and loss of abutting agricultural lands (SEQ Catchments Ltd, 2013). Several months of above average rainfall was experienced prior to the flood of January 2011, which was the first flood Brisbane had seen in the 37 years since the devastating flood of 1974. In contrast, the January 2013 flood was just two years after the January 2011 flood and followed a long period of dry weather.

Therefore, at the start of 2013, catchments for major rural and suburban streams were considerably drier, some even recently burnt, resulting in a faster and greater runoff, as well as significant bank erosion (SEQ Catchments Ltd, 2013). SEQ Catchments Ltd concluded that widespread sediment pollution observed during the January 2013 floods had been exacerbated by the high levels of sediment pollution 'left in the system' following the January 2011 floods.

The weather for the remainder of 2013 was far less extreme. February was wetter than normal in the south east of the state. June was wet in the south east, but dry across the rest of the state. Dry winter months followed, and lead up to the hottest September on record for Queensland. Dry and hot conditions continued in October, and most of November, but there were also numerous and repeated outbreaks of severe thunderstorms. Finally, December was affected by extreme heat, and had the third-lowest rainfall on record, and the lowest since 1938 (Burearu of Meteorology, 2014).

This information on the weather and events that were experienced by South East Queensland from 2008 to 2013 can be used in conjunction with the rank order produced by the MCDM techniques, PROMETHEE and GAIA, to determine if changing climatic conditions affect water quality.

4.2.5.5.2 PROMETHEE and GAIA Analysis of Temporal Variations

There have been many significant weather events in South East Queensland in the past decade. In order to determine if changing climatic conditions have any influence on water quality, PROMETHEE and GAIA were used to rank years 2008 to 2013 in preferential order according to the geometric mean concentrations of all trace elements and heavy metals, compared against the 2011 Australian Drinking Water Guidelines.

The geometric means of the trace element and heavy metal concentrations for all tap water and filtered water samples were considered for this analysis as they are the samples that have been most consistently collected across all six years. These samples were treated at Mt Crosby West Bank WTP and directly consumed by customers in South East Queensland. As a result, raw water and mains water sources were excluded from the 2013 geometric mean concentrations, and reverse osmosis water (2008 only), bottled water and tank water samples were similarly excluded from all years, resulting in the consideration of only tap and filtered water quality.

The pairwise comparison of the geometric mean and guideline concentrations was again facilitated by the V-shape preference function and minimum variable modelling option. Additionally, the preference ranking of the years is based upon the Φ+, Φ- and net Φ values, as described in section 4.2.5.4. Each of these values is shown in Table 4-16.

Table 4-16. Preference Flow table for years 2008 to 2013 ordered from best to worst based on Φ+, Φ- and net Φ values.

Year	Φ+	Φ−	Φ
2012	0.0872	0.0241	0.0631
2010	0.0821	0.0293	0.0528
2008	0.0697	0.0422	0.0275
2013	0.0510	0.0700	-0.0190
2009	0.0493	0.0869	-0.0375
2011	0.0370	0.1239	-0.0869

Preference Flow diagrams depict this ranking of years from most to least preferred as shown by all Φ values in Table 4-16. PROMETHEE I Partial Ranking demonstrates the true ranking of the years, whereas Complete Ranking definitively ranks the years from best to worst. In this case, both ranking methods display the same rank order, shown in Figure 4-42 and Figure 4-43, because all years are comparable to each other.

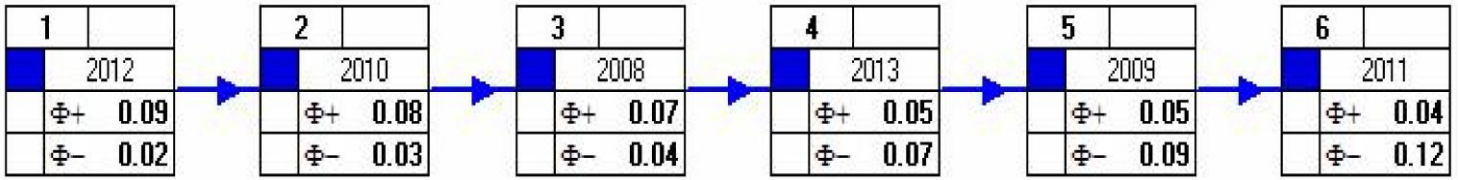


Figure 4-42. PROMETHEE I Partial Ranking of years 2008, 2009, 2010, 2011, 2012 and 2013 against 2011 ADWG.

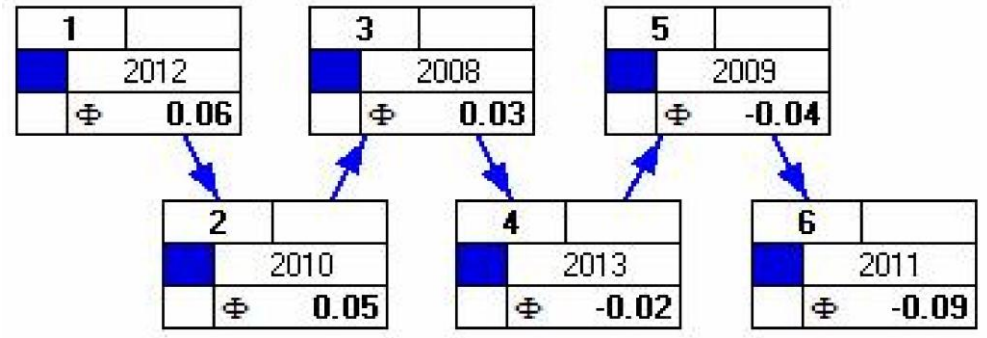


Figure 4-43. PROMETHEE II Complete Ranking of years 2008, 2009, 2010, 2011, 2012 and 2013 against 2011 ADWG.

As seen in Figure 4-42 and Figure 4-43, 2012 is the most preferred year in terms of compliance with the 2011 ADWG. It is followed by 2010, 2008 and 2013. The least preferred years are 2009 and 2011, respectively. It can be seen that the complete rank order is the same as the partial rank order, and both rank orders found that 2012 is the most preferred year, and 2011 is the least preferred year overall.

GAIA was used to find the trace elements and heavy metals (variables) that had the greatest association with each year (object). Based on PCA, a GAIA plot displays the objects and variables, as well as a pi decision axis that points in the direction of the most preferred objects and variables. It is important to note that the data from tuning steps [#1], [#2] and [#3] for each element is combined and represented as one grouped data point on this GAIA plot.

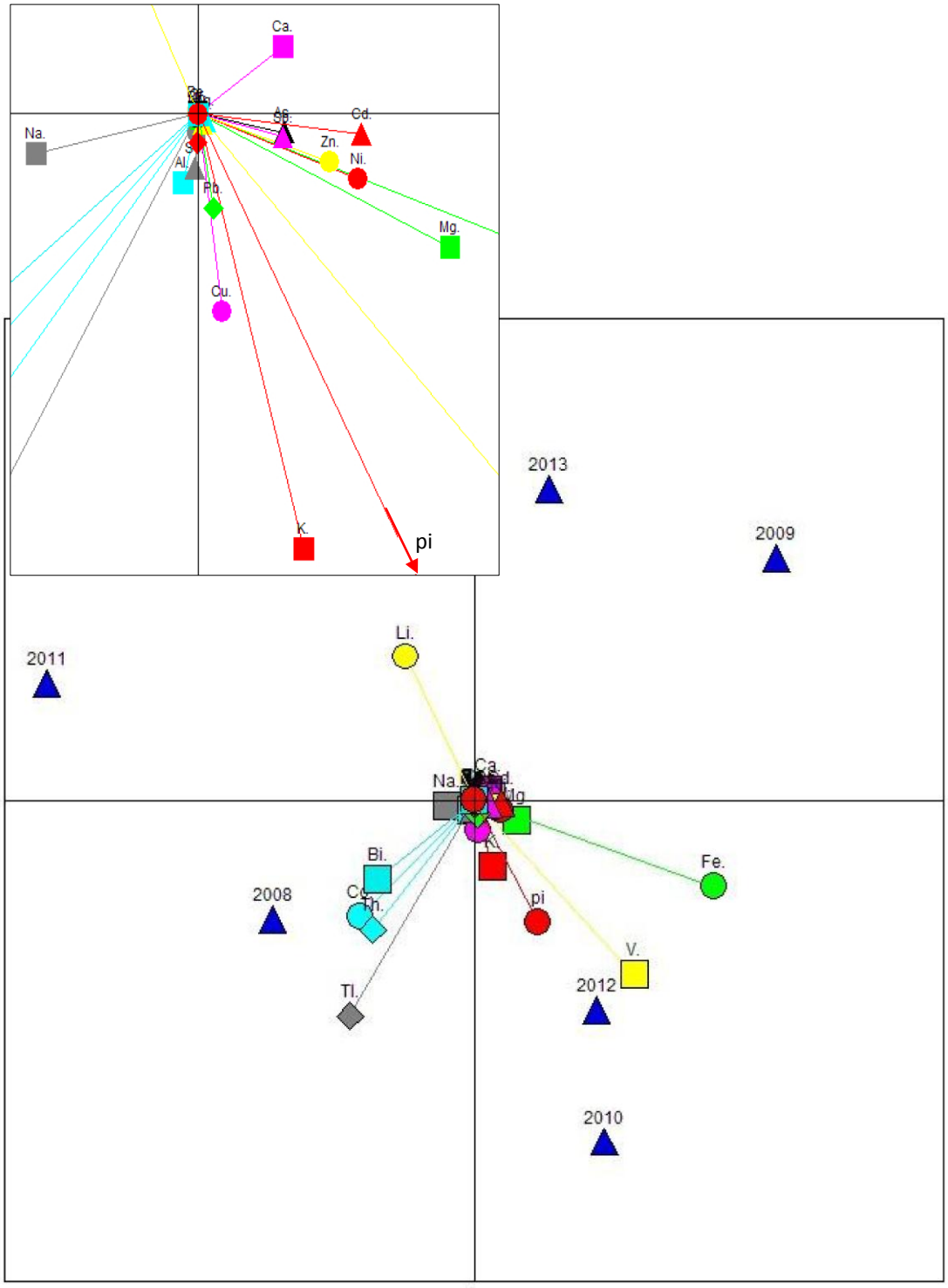


Figure 4-44. GAIA plot (100% magnification) displaying all years and trace elements and heavy metals, positioned based on geometric mean concentrations and ranked against the 2011 ADWG. GAIA plot inset is at 800% magnification around the origin.

Figure 4-44 shows the pi decision axis (red circle) pointing in the direction of years 2012 and 2010. The longer the pi decision axis, the more confidence that can be applied to the decision being made. The pi decision axis seen here is relatively short, indicating some confidence in the decision. Year 2011 is positioned opposite the direction of the pi decision axis, indicating that it is the least preferred year out of all six years analysed in this research. Additionally, the trace elements and heavy metals are not located far from the origin, indicating that they possess a small amount of influence on the decision being made. A total of 86.21% of data variation is shown by the GAIA plot.

The correlation between certain trace elements and heavy metals and each year is more clearly seen at 800% magnification. Iron, potassium, magnesium, vanadium, cadmium, zinc, copper and nickel are correlated with the most preferred years, years 2012 and 2010. Bismuth, cobalt, thorium and thallium are elements with a strong association with year 2008. Calcium is the main element associated with 2013 and 2009. Finally, lithium, present due to anthropogenic sources such as metal alloys and batteries, is the only element with a strong correlation to 2011, the least preferred year in terms of water quality. The majority of trace elements and heavy metals analysed in this research are depicted close to the origin of Figure 4-44. These short vectors therefore indicate that these variables do not have significant influence on the rank order of the years analysed.

The application of the multicriteria decision making methods PROMETHEE and GAIA did not elucidate any clear patterns. As previously mentioned in section 4.2.5.5.1, the most preferred year, 2012, experienced average rainfall with some flooding mixed with severe fire weather. Then, 2010 was this state's wettest year on record. Again, 2008 saw average to below average rainfall, while 2013 experienced a wet start to the year and regional flooding. Queensland experienced below average rainfall in 2009, and severe flooding in 2011.

It was expected that there would be increased concentrations of trace elements and heavy metals in flood waters due to increased run-off into catchment areas that had not seen significant rainfall for years. However, any increase in levels of trace elements and heavy metals may have been negated by the larger volume of water. Similarly, there were no major failures at any water treatment plants in South East Queensland during the periods of flood, therefore drinking water remained in compliance with the 2011 Australian Drinking Water Guidelines.

Overall, the ranking of years does not demonstrate a preference towards drought or flood, or, dry or wet conditions. It can be inferred that over a longer time period, some preference toward a climatic condition may be observed. Alternatively, it may be that there is in fact no discernible preference based solely on trace element and heavy metal concentrations in the water.

Determining the effect, if any, changing climatic conditions have on water quality answers the second question proposed in this research. The application of yet another chemometric technique, Partial Least Squares (PLS) analysis, will provide an answer to the final research question.

4.2.5.6 Partial Least Squares Analysis

The fourth research question (Question IV.) set forth in section 3.1.3 of Chapter Three asks if metal ions can be predictors for water quality. This can be determined through the application of Partial Least Squares (PLS) analysis. PLS involves regression followed by classification, and works with two matrices: **X** and **Y**, and has two objectives, to well approximate **X** and **Y**, and to model the relationship between them (Eriksson et al., 2001). The **X** matrix contains the predictors, while the **Y** matrix contains the responses. The variation in the predictor block, **X**, is summarised by the **X** scores (*T*), and the corresponding variation in the **Y** response block is described by the **Y** scores (*U*). PLS aims to maximise the covariance between *T* and *U* (Eriksson et al., 2001).

The water samples chosen for this PLS analysis were those that were consistently collected and analysed over all six years spanned in this research. These were all tap, tank and filtered water samples. There are a greater number of objects (water samples) than there are variables (trace elements and heavy metals) in this data matrix to be analysed, making it appropriate for PLS analysis by ensuring that over-fitting will not occur.

The data matrix achieved through the ICP-MS analysis of water samples, that is, a matrix of one set of objects and variables, does not fit the standard design required for PLS calibrations. As a result, the variables, the trace elements and heavy metals, were split into two groups, thus forming the **X** and **Y** variable blocks.

The predictor variables that formed the **X** block were chosen because they were the most important variables in this analysis based on Figure 4-45, the PCA loadings plot of all tap, tank and filtered water samples collected in 2013. Additionally, the selection of variables for the **X** and **Y** variable blocks was influenced by the polyatomic interferences experienced by some elements.

For example, based on the positions of selenium and arsenic in Figure 4-45, both elements can be considered important variables; however, they are included in the **Y** response variable block because both ^{75}As and ^{78}Se suffer interference from species $^{40}Ar^{35}Cl$ and $^{38}Ar^{40}Ar^{+}$ respectively. In an attempt to circumvent problems arising from interference, it was decided that these elements would be predicted rather than directly analysed via ICP-MS.

Figure 4-45. PCA loadings plot of tap, tank and filtered water samples collected in 2013. All trace elements, heavy metals and tuning steps analysed are plotted. 48.3% of data variation is shown. X variables chosen for PLS analysis are circled in red.

As discussed in section 4.2.4.1, iron isotope 56 was excluded from analysis due to erroneous results caused by polyatomic interference during analysis of samples via ICP-MS. Despite anomalous concentrations similarly reported for mercury, this element was included as part of the **Y** variable block for PLS analysis. The objective of this inclusion was to determine if concentrations of this heavy metal could be successfully predicted instead of measured, because it has been shown that analysing mercury using the current method applied to all other elements considered in this research produces anomalous results. Finally, chromium isotope 53 and tuning step [#1] for antimony were excluded by the SIMCA P-10.0 software for possessing little to no variance.

The **X** predictor variables and **Y** response variables (inclusive of all tuning steps) are listed in Table 4-17.

Table 4-17. The separation of all trace elements and heavy metals into the X predictor variable and Y response variable blocks.

X Variables	Y Variables
Na, Mg, Al, Ca, V, Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, Tl, Pb, U	**Be, K, Fe, As, Se, Cd, Sb, Ba, Hg, Th**

Therefore, there are a total of 16 **X** variables and 10 **Y** variables. Considering the multiple isotopes analysed for some elements and all tuning steps, overall it can be said that there are 56 **X** variables and 27 **Y** variables.

The aim of this analysis was to use the historical data from 2008 to 2012 as a "work set", and the 2013 data as a "test set" in order to determine if the historical data could be used as a baseline/reference model to accurately predict the concentrations of trace elements and heavy metals found in the tap, tank and filtered water samples analysed in 2013. As a result, classes were assigned based on years and water sources.

Consequently, for historical data, tap water was assigned Class 1, tank water Class 2, and filtered water Class 3, therefore forming the work set. The classes forming the test set were comprised of the 2013 data, and tap, tank and filtered water samples were assigned Class 4, Class 5 and Class 6 respectively. The 2013 test set was then excluded from the historical model for later use as the prediction set. Following the exclusion of the 2013 data, calcium isotope 40 was also excluded due to possessing little to no variance with respect to the 2008 to 2012 work set.

After separating the variables into the **X** and **Y** blocks and assigning classes to form the work set and test set, the data was modelled. There was a total of 13 components produced for this model, all of which were significant (R1 or R2) according to PLS Cross Validation Rules (Umetrics AB, 2005b).

The R^2Y (cum) values represented by the green vertical bars on Figure 4-46 are the cumulative fraction of the variation of the **Y** variable explained after each component. Similarly, the Q^2 (cum) values represented by the blue vertical bars are the cumulative predicted fraction (cross-validation) of the variation of **Y** after each component (Umetrics AB, 2005b).

The model produced displays 65.7% of the data variation of **Y** (R^2Y (cum) = 0.657), with a predictive ability of 44% (Q^2 (cum) = 0.44). The Q^2 value is the main criterion for assessing the quality of the model. Generally, a model with a Q^2 value equal to or higher than 0.3 is statistically meaningful and can be interpreted, a Q^2 value greater than 0.5 is regarded as a good model, while a Q^2 value greater than 0.9 indicates an excellent model (Sun, 2004). Therefore, the predictive ability of this model can be considered good and further investigations can continue.

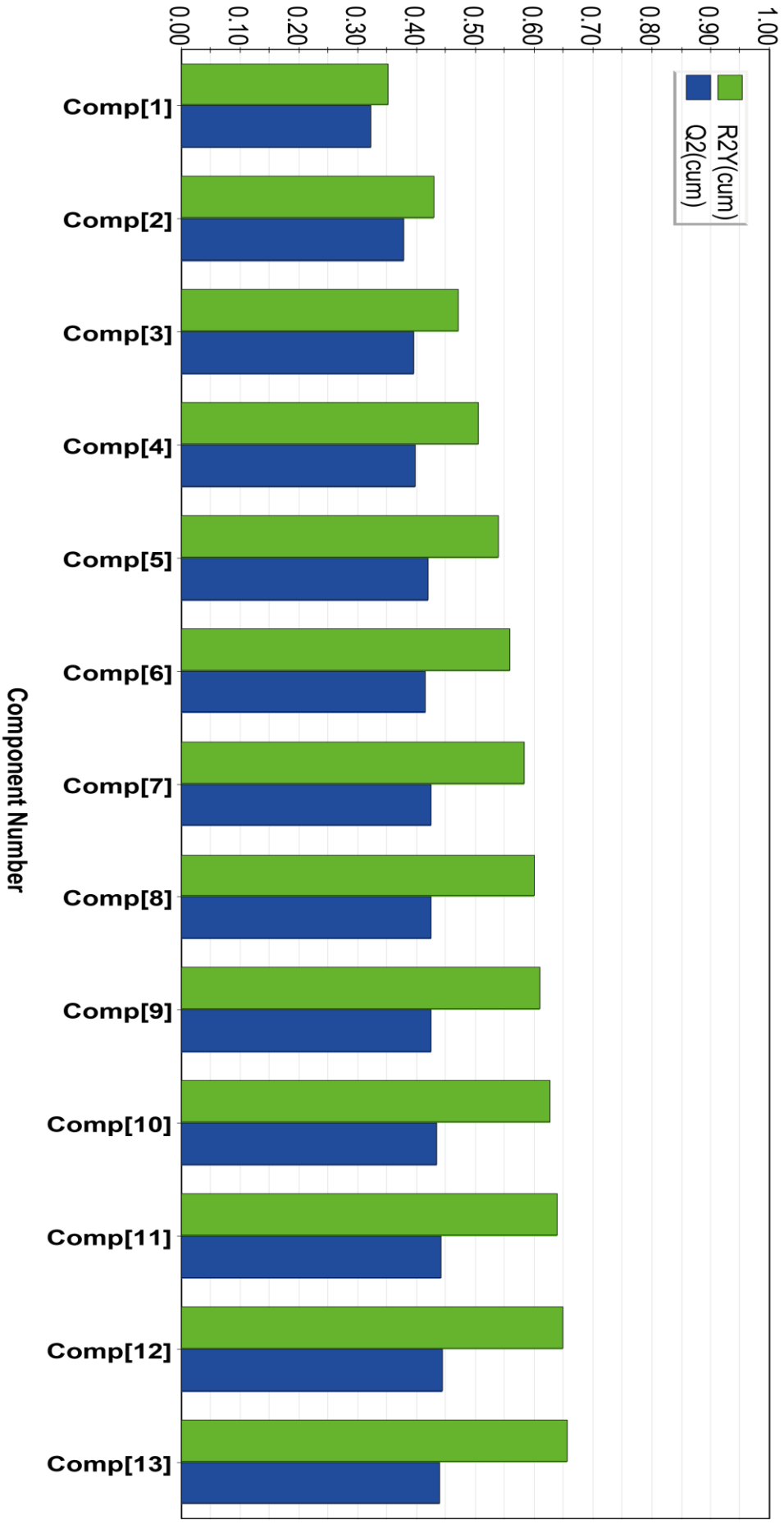


Figure 4-46. The model overview plot demonstrates the R2Y (cum) and Q2 (cum) values for all 13 significant components fitted to this model.

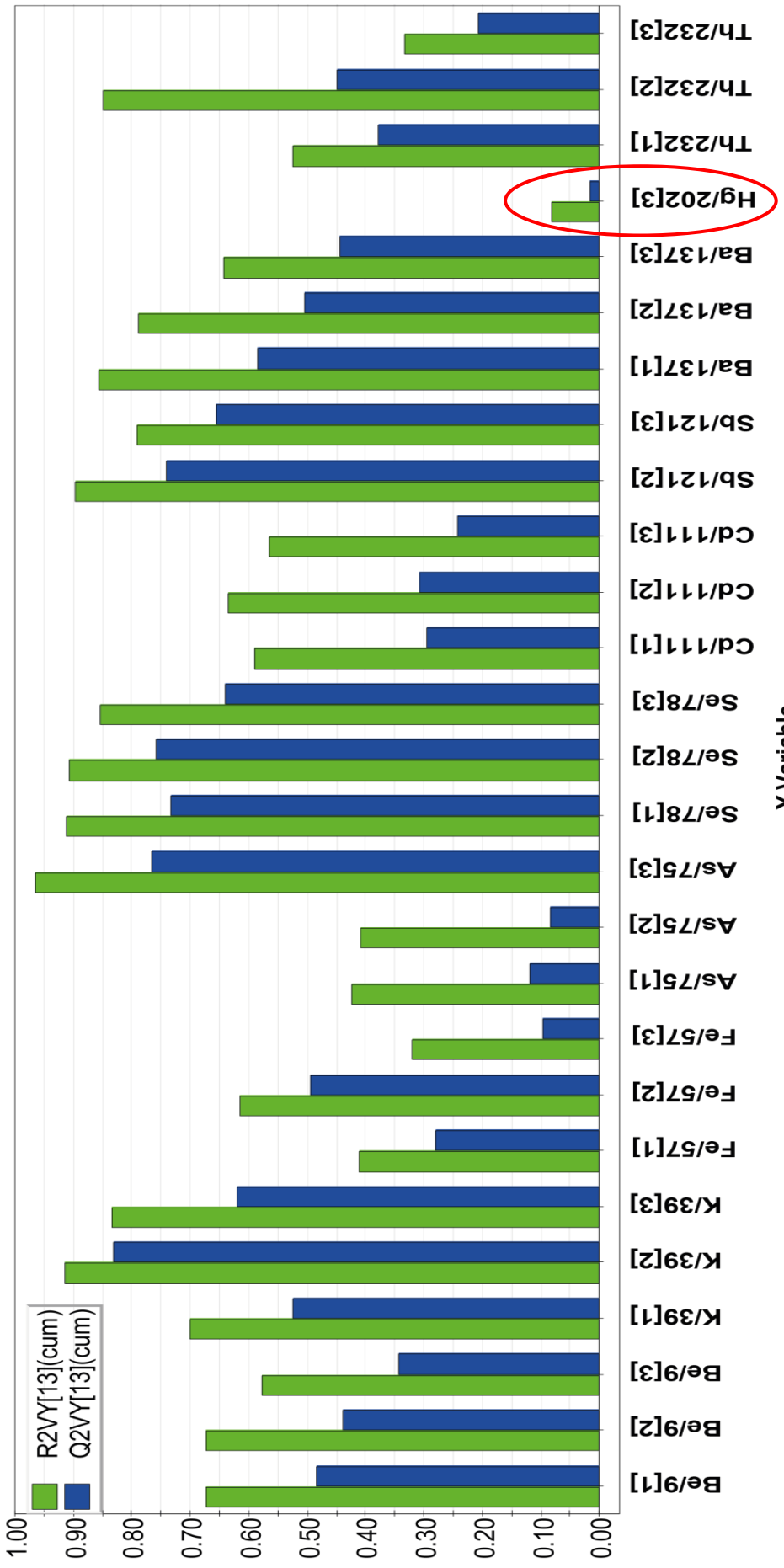


Figure 4-47. The X Y Overview bar graph for this PLS model shows the contribution to the data variance of Y (R^2Y) and the predictive ability (Q^2) of each element by the green and blue vertical bars respectively.

The overview of this model in terms of the **Y** response variables is depicted in Figure 4-47. The green bars represent the R^2Y values or the contribution to the variance of **Y** made by each element; the blue bars indicate the predictive ability of each element (and tuning step) in this **Y** response block. The contribution to the data variance and the predictive ability (or the ability to be predicted) of most trace elements and heavy metals is significant.

The exception to this is the heavy metal mercury (circled red in Figure 4-47). The contribution to variance and predictive ability demonstrated by mercury is the lowest of any element. Previous analyses performed on all raw data, historical and current, showed anomalous results were produced by the ICP-MS analysis of mercury. Therefore, it was resolved that, despite its low predictive ability, it would be advantageous to predict mercury concentrations in water samples, as the current method of analysis has produced erroneous results.

In addition to the contributions of the **Y** response variables, the importance of all tuning steps of the trace elements and heavy metals in the **X** predictor block is displayed in Figure 4-48, the variable importance in the projection (VIP) plot.

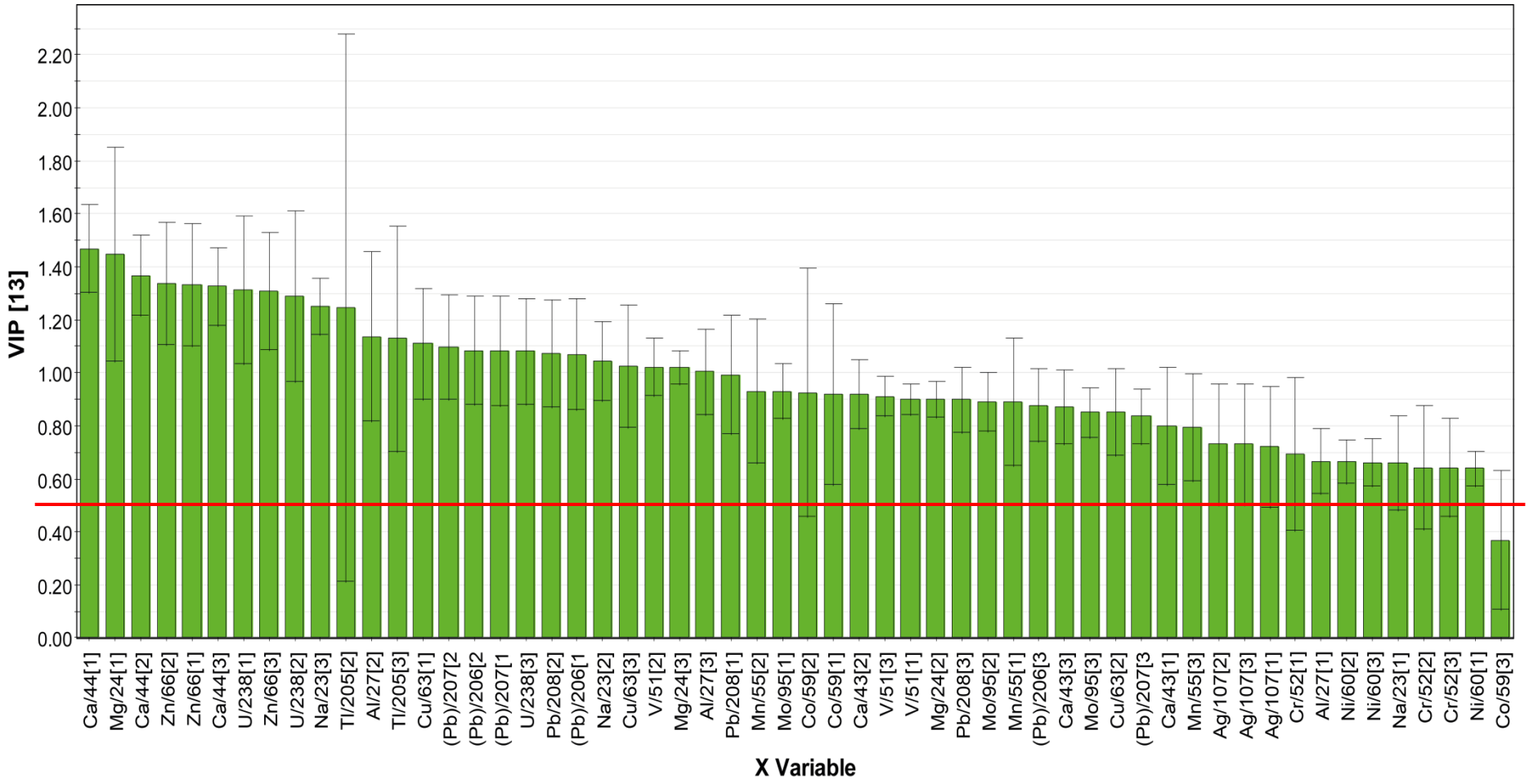


Figure 4-48. This VIP plot considers all 13 components of this model and demonstrates which X predictor variables have the greatest influence on Y. The red line indicates 0.5, any variables below this line are of the least importance.

This VIP plot estimates the influence of every **X** predictor variable on the **Y** response block. Variables with larger VIP values are the most relevant for explaining **Y**, and those with VIP values below 0.5 are the least important (Sun, 2004).

Figure 4-48 shows that tuning step [#3] of cobalt is the least important variable when it comes to influencing the **Y** response variables. All other elements and tuning steps have significant influence on the **Y** response block. The top three most important variables are calcium, magnesium and zinc.

After examining the contributions, predictive ability and influence of the **X** and **Y** blocks, a scores plot of the objects was created for the first two components for both the **X** (*T*) and **Y** (*U*) blocks respectively. The **X** (*T*) scores plot demonstrated the most useful information, and shows how the objects (tap, tank and filtered water samples from 2008 to 2012) are situated with respect to each other.

PLS shows the differences in the data, not just variance, hence the results achieved with PLS scores plots are different to the results of Principal Component Analysis. Several scores plots were constructed to investigate the relationships between the **X** and **Y** variable blocks and the historical water samples (objects) included in the work set.

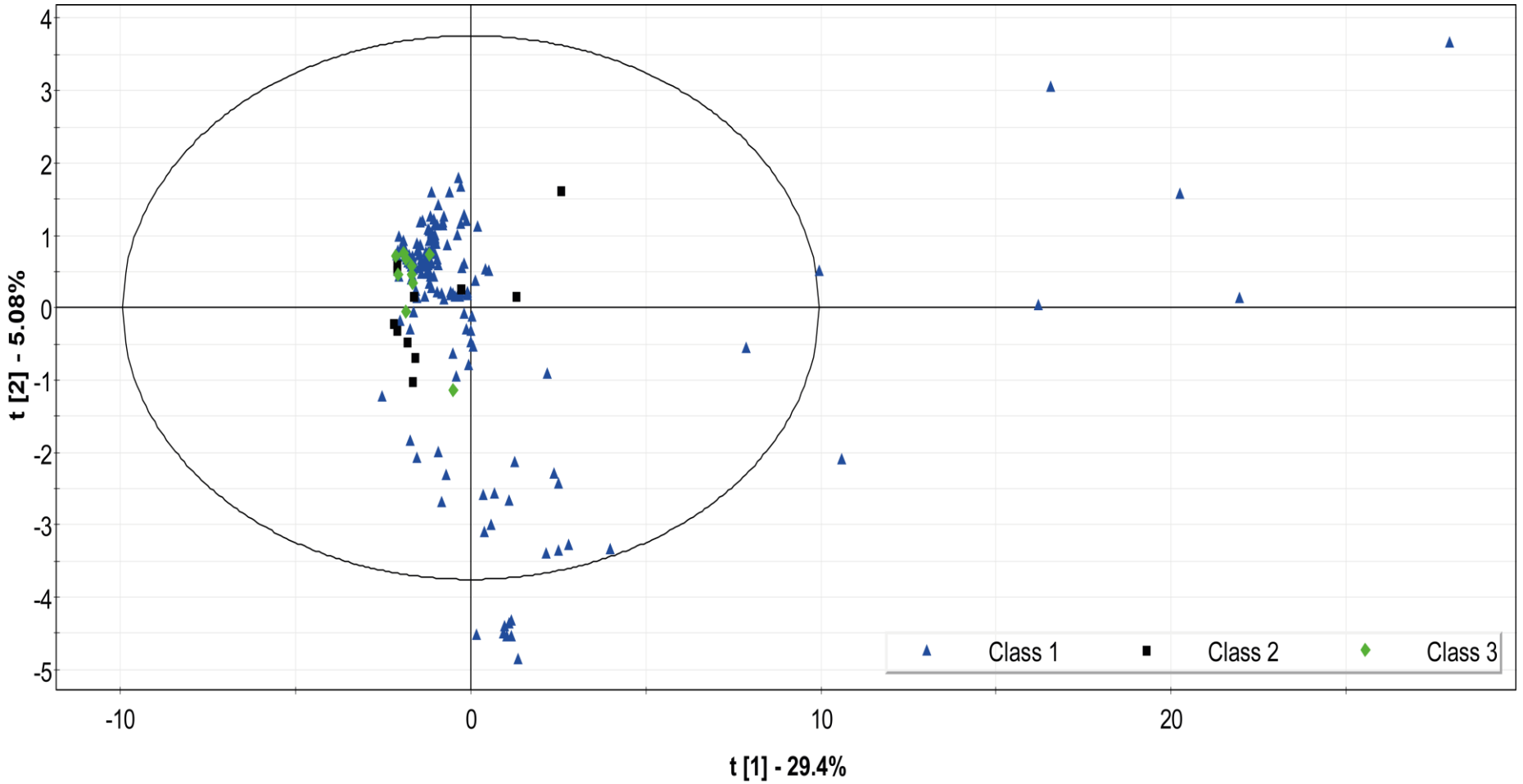


Figure 4-49. PLS plot of X scores (T) demonstrating 34.48% of data variance and showing some separation according to classes specified in the work set. Wok set classes 1, 2 and 3 are tap, tank and filtered water samples respectively, and are coloured according to the legend (inset).

The variation in the **X** predictor block is summarised by the **X** scores (*T*). Figure 4-49, the *T* scores plot of the first two components, demonstrates some clustering of classes as specified in the 2008 to 2012 work set.

The result shown in Figure 4-49 is different to that of Figure 4-6, the PCA scores plot where all sample data plotted clustered according to year collected rather than water source type (i.e. tap, tank or filtered). This is indicative of the difference between these PLS and PCA techniques, where the difference in the data versus the variance in the data is depicted respectively. As a result, it can be concluded that tap, tank and filtered water sources are indeed different, as previously confirmed by PCA batch by batch analysis.

The variation in the **X** predictor block is represented by **X** scores, *T*, and the corresponding variation in the **Y** response block is described by the **Y** scores, *U*. Therefore, a combination of the **X** and **Y** scores is depicted by plotting component one of each block, *T* and *U*, in Figure 4-50, to assess the goodness of fit of the model.

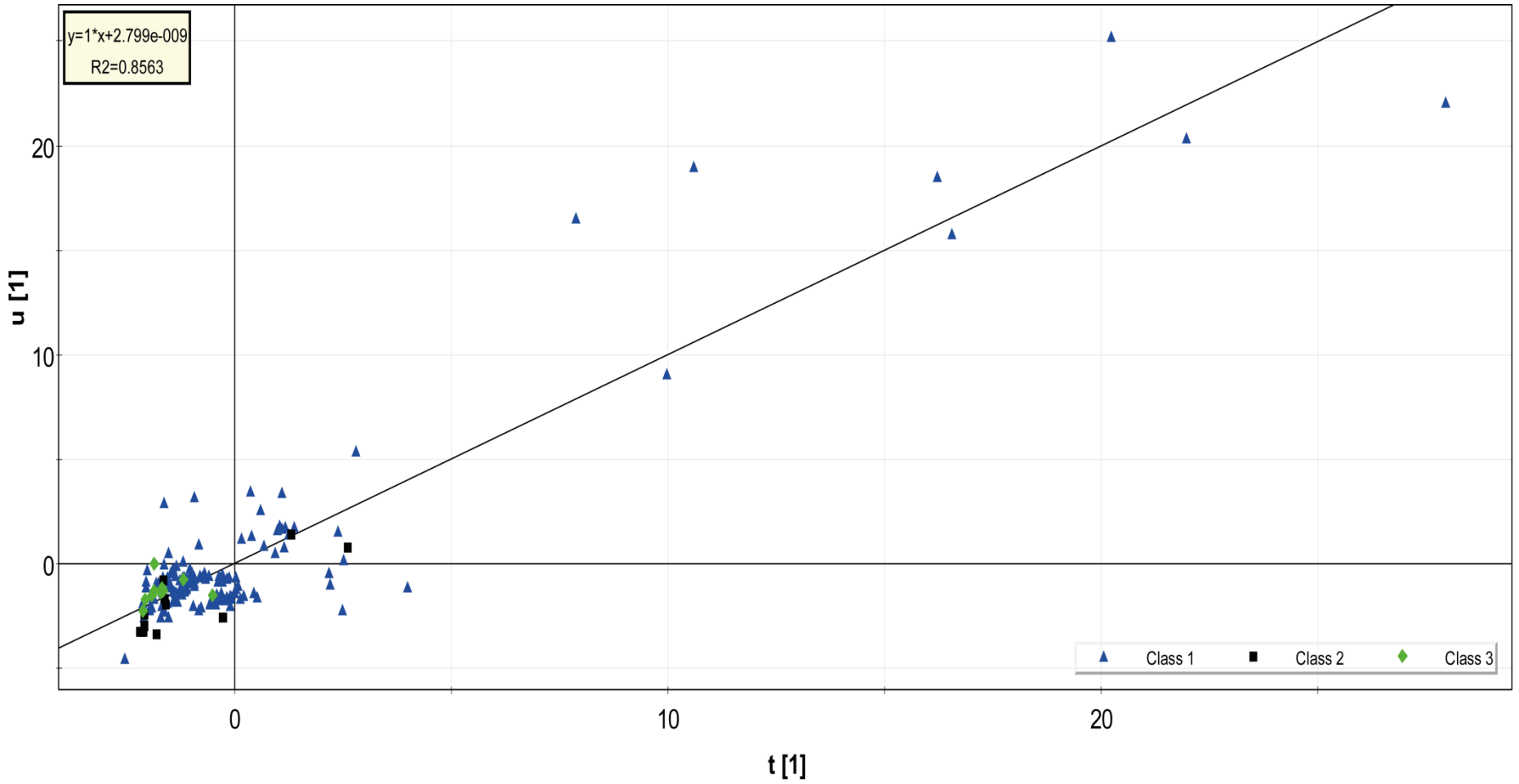


Figure 4-50. PLS scores plot of the first components of both X and Y variable blocks; the line of best fit, corresponding equation and correlation coefficient are also shown. Wok set classes 1, 2 and 3 are tap, tank and filtered water samples respectively, and are coloured according to the legend (inset).

Figure 4-50 displays the relationship between **X** and **Y**. This scores plot demonstrates that the model is a good fit due to the small scatter around the straight line. Additionally, the straight line through the data has a high correlation coefficient (R^2) of 0.8563.

Finally, a weighted loadings plot, Figure 4-51, was created and displays the correlations between the **X** predictor variables and the **Y** response variables.

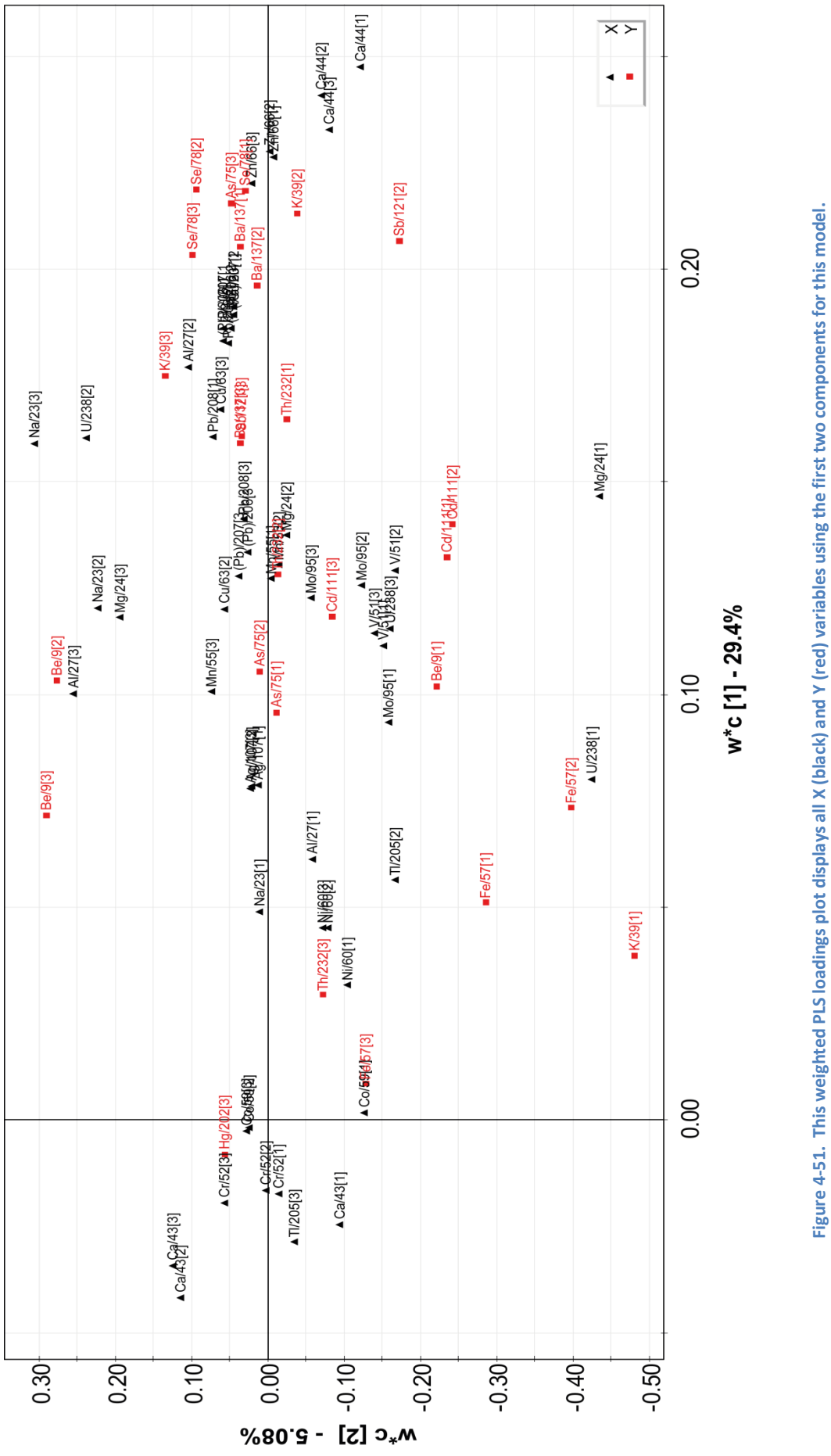


Figure 4-51. This weighted PLS loadings plot displays all X (black) and Y (red) variables using the first two components for this model.

The weights for the **X** variables, w*, indicate the importance of these variables and are related to the correlation between the **X** variables and the **Y** scores *U*. Similarly, the weights for the **Y** variables, c, combine the **Y** variables to form the scores *U* (Umetrics AB, 2005b). Therefore, a w*c plot shows the relationships between **X** and **Y** variables, the **X** variables which are most important, and which **Y** variables are related to which **X** variables.

The combination and positioning of the **X** and **Y** variables therefore demonstrates these relationships. Examples from Figure 4-51 show that zinc is related to selenium, and that cobalt and chromium are related to mercury. It can also be seen that calcium and zinc are the **X** variables furthest from the origin of this loadings plot, indicating that these elements have the most influence in this model. This inference is supported by the results of Figure 4-48, where calcium and zinc were listed in the top three most important variables.

After examining the relationships between the **X** predictor variables and the **Y** response variables, as well as the *T* and *U* scores, this PLS model was validated. In accordance with works done by Ayoko et al. (2007) and Eriksson et al. (2001), this model was validated by creating several parallel models in which the **X** variables stayed the same and the order of the **Y** variables was randomly permuted 200 times. Separate models were then fitted to all the permuted **Y** variables, similarly extracting all 13 components of the original matrix. New values of R^2Y and Q^2Y computed from permuted data were then compared with the R^2Y and Q^2Y values from the original PLS model in order to appraise the statistical significance of the original model (Ayoko et al., 2007).

An example of the 200 permutations performed for each **Y** variable is shown by Figure 4-52 for selenium (isotope 78, tuning step [#3]).

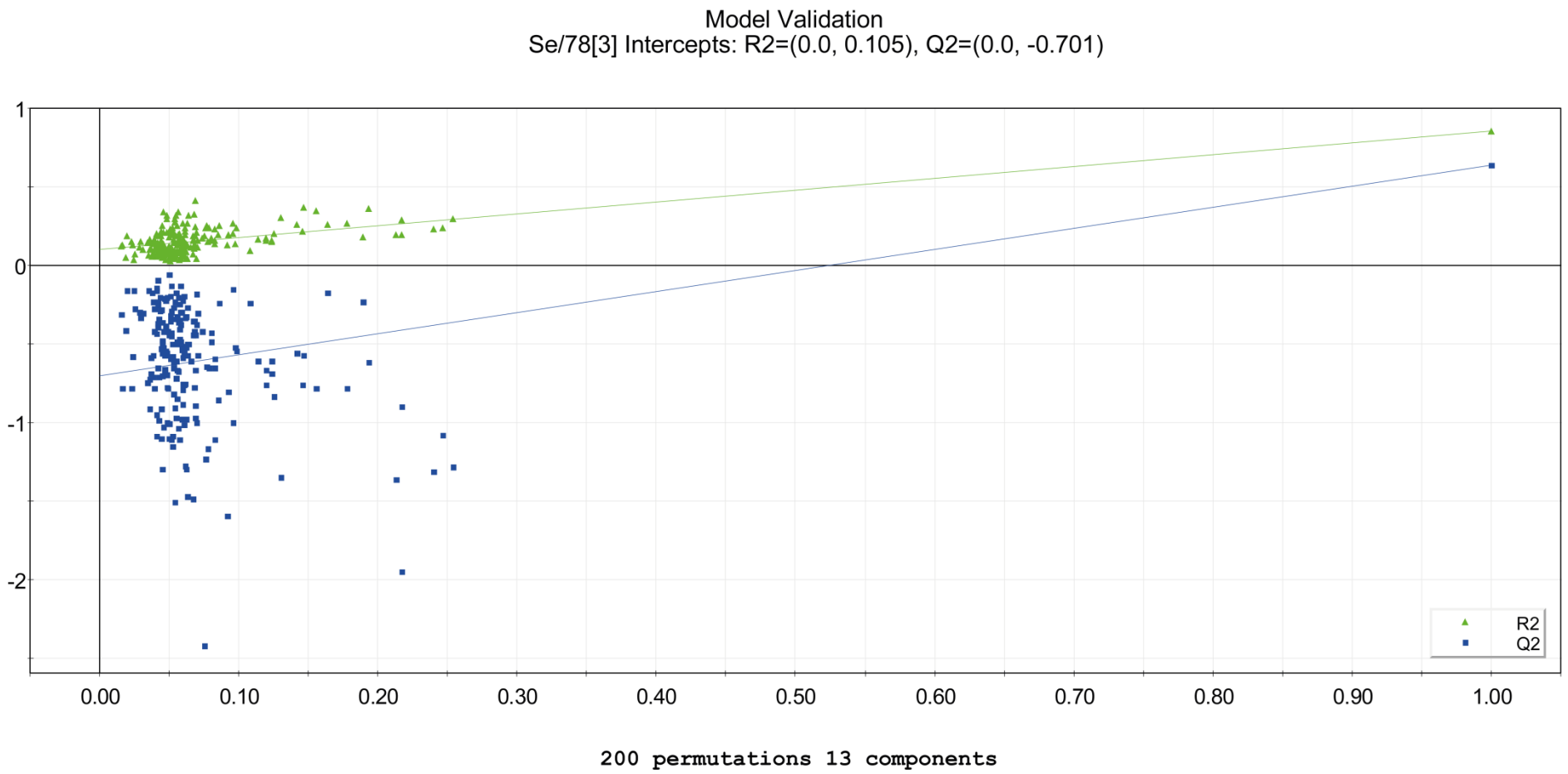


Figure 4-52. This plot for selenium (isotope 78, tuning step [#3]) demonstrates the 200 permutations for 13 components, where the R^2 values are green (triangles) and the Q^2 values are blue (squares). The x axis represents the correlation coefficient and the y axis represents the cumulative R^2 and Q^2 values.

This plot displays the correlation coefficient between the original **Y** and the permuted **Y** response variables (x axis) against the cumulative R^2 and Q^2 values (y axis), and draws a regression line for the 200 permutations extracted from the 13 components of the original data matrix. It can be seen that the R^2 and Q^2 values for this plot are 0.0939 and -0.364 respectively.

This process was performed for all tuning steps of all trace elements and heavy metals in the **Y** response variable block. The new R^2 and Q^2 values for all elements can be seen in Table 6-8 in Appendix C-4. The permuted data always gave R^2 and Q^2 values lower than the original model, where $R^2Y = 0.657$ and $Q^2 = 0.44$. The remodelled R^2 values ranged from 0.0855 to 0.126, and the remodelled Q^2 values were all negative, ranging from -0.829 to -0.121.

As a result, it was confirmed with confidence that the original PLS model was significant. Additionally, Eriksson, et al. (2001) have previously shown that if remodelled values of $R^2 < 0.3\text{-}0.4$ and $Q^2 < 0.05$, then the explanatory and predictive powers of the original model are higher than that of the parallel models. This is the case for the randomly fitted **Y** data. Therefore, the present PLS model is valid.

Finally, Observed vs. Predicted plots were constructed for each tuning step for each element in the **Y** response block. Using all 13 original components, these plots graphed the observed values against the predicted values of all objects, or water samples, collected in 2013 that were earlier excluded as the test set (or prediction set). The observed value is the measured value of the original variable, and the predicted value is the variable value predicted for that observation (Umetrics AB, 2005b).

The R^2 values from the linear trend line and the root mean square error of prediction (RMSEP) values for each element are given on each plot. An example of an Observed vs. Predicted plot is shown by Figure 4-53 for the same example element, selenium (isotope 78, tuning step [#3]).

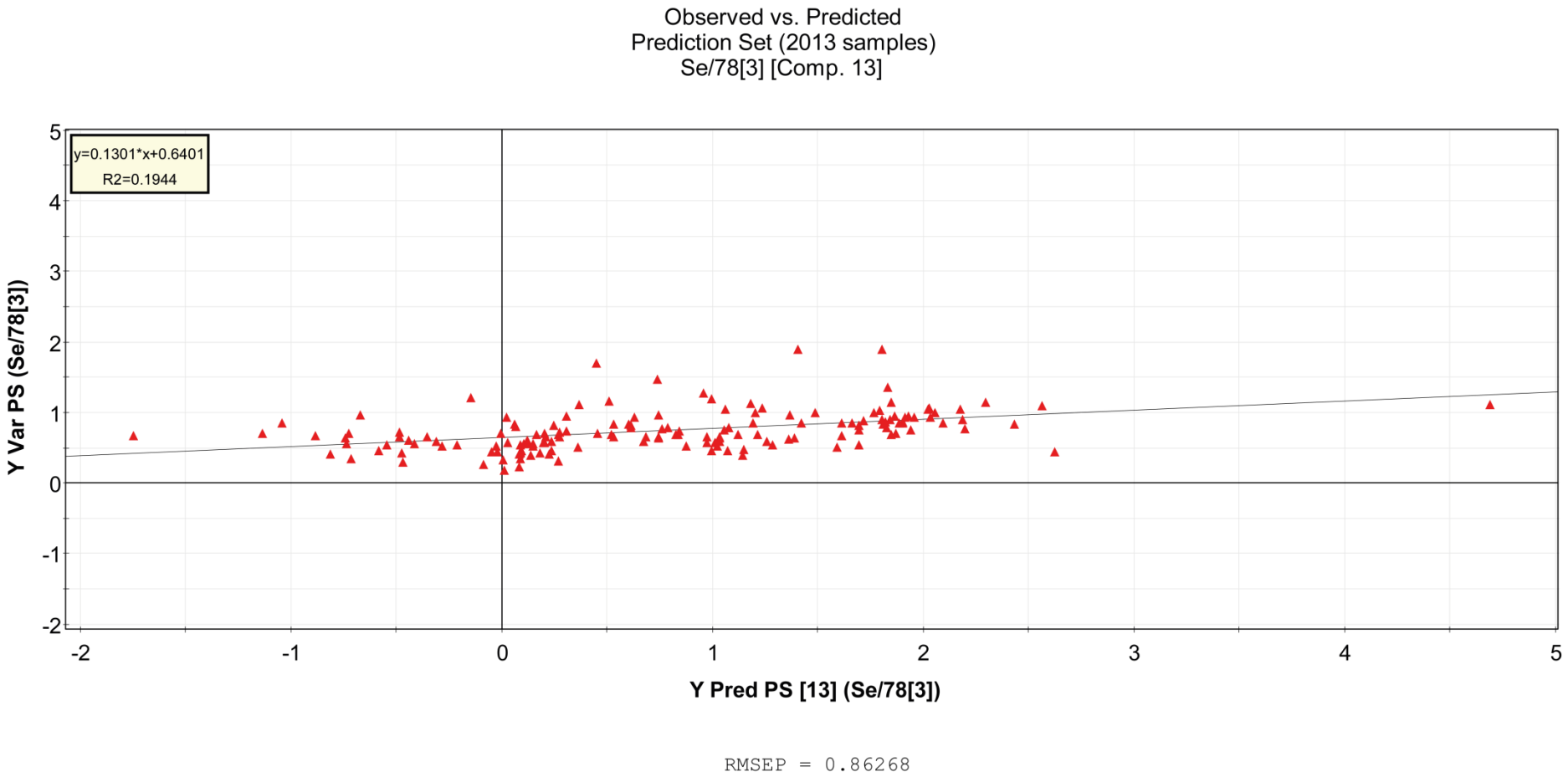


Figure 4-53. This Observed vs. Predicted plot for selenium (isotope 78, tuning step [#3]) shows the positioning of all objects in the 2013 test set (or prediction set) based on the observed and predicted values for this Y variable. A linear trend line, corresponding equation and correlation coefficient (R^2) are shown, as well as the RMSEP value.

The R^2 and RMSEP values for each element and tuning step were tabulated and are presented in Table 6-9 in Appendix C-4. The root mean square errors of prediction that may have evolved from errors in the work set, errors in the test set or errors in the prediction, are relatively low for the trace elements and heavy metals of the **Y** response variable block.

The exceptions to this are potassium, iron, barium and mercury, whose RMSEP values are comparatively high. It can be inferred that the errors associated with predicting mercury concentration values for water samples collected in 2013 stem from the earlier assertion that the sample preservation method (applied in 2013 only) and analysis via ICP-MS resulted in anomalous concentration values for this heavy metal across all six years of this longitudinal study.

Following the examination of relationships between the **X** predictor variables and the **Y** response variables, and the validation of the model by response permutation, it can be concluded that the PLS model developed is able to predict quantitative results for future work, as demonstrated by the 2013 test set. The R^2, Q^2 and RMSEP values that were achieved by modelling and cross-validating this water quality data indicate that the model used in this research meets the criteria for acceptable PLS models according to Sun (2004) and Eriksson et al. (2001).

Furthermore, this PLS model may still be refined, and as more years of data are collated, more years can be added to the work set (currently containing the 2008 to 2012 historical data) to more accurately predict the concentrations of trace elements and heavy metals in various water sources.

Therefore, the use of PLS analysis to model trace element and heavy metal concentrations as a vital aspect of water quality has shown that metal ions can be used to predict other metal ions of interest. Therefore, creating and validating this PLS model answers the fourth and final question posed in this research, by establishing that metal ions can indeed be predictors for water quality.

Chapter Five: Summary and Conclusions

This chapter outlines the conclusions and significant outcomes of this research. A summary of the importance of this research and the methodology used to achieve the results is provided, as well as clear answers to each of the research questions posed in this thesis. The contribution to knowledge and practical implications of this research are also discussed. Finally, the limitations encountered in this study, and recommendations for future work that may be conducted as an extension of this research are also outlined.

The purpose of this research was to investigate the concentration of trace elements and heavy metals in potable water of the greater Brisbane area. This research is important because while there have been extensive studies into the health of natural water bodies, there has been no analysis of water quality at the consumers' tap. Regular maintenance and monitoring of water quality is required, as it verifies that the operation of the water supply system and the treatment barriers implemented to supply safe drinking water are functioning satisfactorily. Alternatively, any trends or problems with the water supply system that may have gone unrecognised can be identified. For example, Queensland Urban Utilities conducts monthly monitoring and are planning a $45 million program of work to replace kilometres of water mains over the next three years in order to improve the efficiency and reliability of the water network (Queensland Urban Utilities, 2013a). Overall, monitoring provides consumers with confidence that the quality of water in the distribution system, as supplied to the consumer, is meeting guideline values and agreed levels of service (National Health and Medical Research Council, 2011).

Potable water quantity and quality is regulated by local governing bodies in accordance with the 2011 Australian Drinking Water Guidelines. The trace element and heavy metal content of water is a vital aspect of water quality. There is a fine balance between beneficial and harmful levels of many trace elements and heavy metals required for human health. The daily consumption of significant volumes of water makes drinking water an important pathway for a wide range of these elements to enter the body. Currently, the responsibility of the water supplier typically ends at the water meter. The National Health and Medical Research Council (2011) state that water quality should be managed up to the

point of consumption to account for water quality changes that may arise as a result of the internal plumbing arrangement on customer properties.

Water quality can deteriorate within buildings due to poor design and management of internal plumbing systems, where incompatibility between the chemistry of supplied drinking water and plumbing fittings can impact water quality (National Health and Medical Research Council, 2011). Common issues can include water softness or hardness, cupprosolvency and plumbosolvency; additionally, water that sits unused in pipe networks for extended periods of time may have elevated levels of metals. Therefore, this research was undertaken to examine the water quality at the consumers' tap, and to investigate the changes that occurred between the treated water leaving Mt Crosby West Bank WTP and arriving at homes in the greater Brisbane area.

The analysis of trace elements and heavy metals was achieved through Inductively Coupled Plasma – Mass Spectrometry and four different chemometric techniques: PCA, HCA, PROMETHEE and GAIA, and PLS. This longitudinal study covered a six year span. There were 218 water samples collected and analysed by undergraduate students from 2008 to 2012, and 226 samples were personally collected and analysed in 2013 specifically for this research. A total of 444 tap, tank, filtered, bottled, raw, treated and distribution mains water samples were analysed for a suite of 26 trace elements and heavy metals across three tuning steps (the result of collision/reaction cell conditions) with ICP-MS.

The ICP-MS method applied in this research was based on US EPA Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry. The multi-element capability of ICP-MS and its ability to handle complex sample matrices, such as water, are considered major advantages of the instrument. As a result, all 26 elements of interest could be analysed at once, and no sample preparation procedures were required. Student samples from 2008 to 2012 were analysed batch by batch upon collection, and no sample preservation procedures were performed. Samples collected in 2013 underwent filtration, acidification and refrigeration for preservation purposes.

The quantitative results achieved through ICP-MS were analysed first as raw data in comparison to the 2011 ADWG. Many consumers equate aesthetics with the safety of drinking water, hence aesthetic guideline values, which are lower than the associated health guideline values, were used whenever possible. Almost all trace elements and heavy metals of interest for all samples analysed were within the aesthetic guidelines of the 2011

ADWG. Elements that exceeded aesthetic guideline values, such as iron and copper, were often attributable to household plumbing systems; however, the higher health guidelines were rarely exceeded. Various chemometric techniques were then used to investigate the variance, similarity, difference, predictive ability and preferences within the water quality data in order to answer the four questions posed in this research.

The research conducted in this thesis achieved answers to each of the four research questions and led to several significant outcomes.

Firstly, for the purpose of Question I.a., treated water and raw water collected in 2013 were defined as tap water that had undergone rigorous treatment processes (coagulation, flocculation, sedimentation and filtration) at Mt Crosby West Bank WTP, and as raw water that had not undergone any kind of treatment, respectively. Through Principal Component Analysis (PCA), it was seen that raw water was distinct from treated water, where almost all raw water samples appeared as outliers in comparison to tap water samples. Consequently, considering the extensive treatment of potable water in contrast to no treatment for raw source water, it can be concluded from these results that raw water is indeed distinguishable from treated water.

Water's journey from Mt Crosby West Bank WTP through the supply network to consumers' taps was expected to have an effect on the concentrations of trace elements and heavy metals present in this resource. The levels of elements were expected to increase as this journey progressed. This was investigated by comparing 2013 raw data from water samples taken at different points throughout this journey (Question I.b.). Firstly, the quality of treated water from the Cameron's Hill reservoirs was compared to mains water samples collected at different points throughout the water distribution system. Out of the suite of 26 elements analysed, concentrations of almost all trace elements and heavy metals were greater in the mains water samples, with the exception of molybdenum, silver and uranium.

Subsequently, the quality of mains water and tap water was compared. Again it was seen that concentrations of trace elements and heavy metals in mains water samples were generally higher. However, concentrations of copper and zinc were higher in tap water samples, and concentrations of lead, iron, nickel and cobalt in tap water samples were extremely close to those in mains water samples. The aforementioned elements are all prominent in household pipes and plumbing fixtures, therefore lending credibility to these

results, and to the assumption that concentrations of trace elements and heavy metals would increase between leaving Mt Crosby West Bank WTP and arriving at consumers' taps.

Additionally, potable water testing of mains water is conducted by Seqwater and Queensland Urban Utilities (via SAS Laboratory). These water quality reports were used as an external point of comparison for this research. The geometric means of the trace element and heavy metal concentrations in all potable waters analysed in 2013 were compared to both reports. It was found that levels of magnesium, calcium, iron, copper, zinc and lead tested higher for this research than the independent report averages. The differences among the highlighted elements could be attributed to water hardness, and the composition of the water distribution pipes, household pipes and plumbing fixtures. From the results of this analysis, it can be concluded that concentrations of trace elements and heavy metals do indeed change from leaving Mt Crosby West Bank WTP to arriving at consumers' taps.

Next, chemometric technique PCA was used to analyse multiple combinations of potable water samples collected as historical data and current data. When analysed batch by batch, historical data clustered according to water type, i.e. tap, tank, filtered and bottled water. Similarly, when samples collected in 2013 were analysed in various combinations, it could be seen that tap and filtered water samples were very closely related. This is a logical outcome and is the result of these water types taking the same pathway to the consumers' taps, differing only slightly when filtered water was diverted to a different tap or filtering unit. More separation was displayed between tap and tank water samples. Tank water can be described as rain water that lands on the roof, and is transported through gutters and downpipes, and stored in metal, plastic, or concrete tanks. Therefore, the routes taken by tap and tank water samples are very different, a fact that helps to explain the observed PCA results. Finally, bottled water was also distinct from tap water, where bottled water samples appeared as outliers in comparison to tap water samples, similar to what was seen in the earlier comparison of treated water and raw water samples.

Concurrently, the trace elements and heavy metals associated with each of these water types were investigated through the use of PCA loadings plots. For example, it was found that tap water had strong associations with macroelements sodium, magnesium, potassium, calcium and iron; whereas tank water samples were associated with manganese, zinc, lead, silver, chromium, cadmium, cobalt and nickel. From the thorough

investigation of various combinations of potable water samples, it was concluded that different potable water sources could be distinguished by chemometric analysis of their trace element and heavy metals concentrations, thereby answering Question I.c.

Tap water samples collected in 2013 were also analysed separately by PCA. The clustering observed was found to match suburb areas from which the samples were collected. This level of distinction was considered an excellent result and a significant finding. The detectable differences in trace element and heavy metal concentrations between suburbs was believed to be the result of the distance the water had travelled through the mains water distribution system, as well as the age of the area's development and therefore the age of the distribution pipes. Earlier analysis of raw tap water and mains water data also showed generally lower concentrations of all trace elements and heavy metals present for new housing estates. Additionally, research demonstrated that raw water sources are mixed both at Mt Crosby West Bank WTP and within the SEQ Water Grid. As a consequence of this mixing, it was concluded that the original raw source of the water cannot be determined from the trace metals profiles of potable water samples (Question I.d.). As a result of all analyses described above, it was concluded that the trace element and heavy metal fingerprints of all water sources analysed could be distinguished (Question I.).

To answer Question II., chemometric techniques PROMETHEE and GAIA were used to rank each year of this longitudinal study based on the geometric means of the trace element and heavy metal concentrations of potable water samples, in comparison to the 2011 ADWG. The weather patterns experienced throughout each year, as well as any significant events, i.e. floods, fires, etc., were also researched. These multicriteria decision making methods were used to determine if changing climatic conditions affect potable water quality. However, the ranking of years 2008 to 2013 did not demonstrate any preference toward wet, dry or extreme climatic conditions. It was noted that despite any extreme climatic conditions, such as the floods experienced in 2011 and 2013, there was no disruption to the treatment processes at Mt Crosby West Bank WTP. As a result, drinking water remained in compliance with the 2011 ADWG. From the outcome of this analysis, it was inferred that perhaps over a longer time period, some preference toward a climatic condition may be observed. Alternatively, it could be concluded that there is in fact no discernible preference based solely on trace element and heavy metal concentrations in the water.

All six years of data were also used in PLS analysis to determine if metal ions could be predictors for water quality (Question IV.). Potable water data from this longitudinal study was separated into a work set and test set, and classes were assigned according to water source type (tap, tank and filtered water). Trace elements and heavy metals were also separated into **X** and **Y** variable blocks. The 2008 to 2012 data were modelled using the **X** predictor variables, and the model explained 65.7% of the data variance of **Y** and had a predictive ability of 44%. Analysis revealed some class clustering of the samples, and the relationships between the **X** and **Y** variables were demonstrated when plotted together on a weighted loadings plot. The R^2, Q^2 and RMSEP values that were achieved by modelling and cross-validating this PLS model with the current 2013 water quality data (originally excluded as the test set) indicates that the model used in this research is an acceptable PLS model. The chosen **X** predictor variables were able to predict the concentrations of the trace elements and heavy metals that were designated as **Y** response variables. Therefore, from the construction of a valid model, it can be concluded that metal ions can be predictors for water quality. In future research, as more years of data are added to this model, it may be refined to use fewer **X** predictor variables, and to improve the predictive ability of this existing model.

Lastly, all chemometric techniques employed in this research provided valuable information over and above what can be achieved by the analysis of raw data alone. Principal Component Analysis (PCA), Hierarchical Cluster Analysis (HCA), multicriteria decision making methods PROMETHEE and GAIA, and Partial Least Squares (PLS) analysis were the techniques used in this research to maximise the elucidation of information collected from the data (Question III.) and answer the questions posed in this research. Additional information that was not directly related to any of the questions posed in this research was gained from PCA, HCA and PROMETHEE and GAIA analyses. For example, further investigations into the relationships among bottled water samples and among raw water samples were performed using multiple techniques. The similarities between bottled water brands and between raw water sources were analysed via HCA. Then, the most preferred raw water source in South East Queensland was determined by using PROMETHEE and GAIA to rank all raw water sources based on their trace element and heavy metal concentrations against the ANZECC/ARMCANZ (2000) water quality guidelines for toxicants. Qualitative survey data regarding pipe type was also transformed into categorical data and, along with all tap water samples collected in 2013, was analysed via PCA to gain insight into the elements associated with household PVC and copper pipes.

This research is the first known study of potable water quality at consumers' taps in the greater Brisbane area. There is little, if any, literature covering the collection and analysis of potable water on the scale undertaken in this research. Established methodologies and guideline values were used for this analysis of trace element and heavy metal concentrations in waters. Therefore, the contribution to knowledge is the coupling of ICP-MS analysis with various chemometric techniques to identify water sources and sources of contaminants, in addition to determining the use of metal ions as predictors for water quality.

The results achieved in the course of this research have answered all research questions proposed and led to the aforementioned conclusions. The resulting practical implications of this research include the ability to use a reduced number of water quality parameters to identify water sources in analyses coupled with the application of chemometric techniques. The coupling of chemometric and analytical techniques does indeed maximise the elucidation of information from data, and can be practiced in a wide variety of research and industrial applications. In particular, PLS analysis has the potential to make water quality testing faster and more cost-effective by analysing a reduced number of variables. As a result, the model developed in this research may be applied in industry by water authorities. Additionally, as yearly data is continually collected, the predictive ability of the model is likely to increase, consequently increasing the accuracy of results predicted.

Similarly, the continued collation of yearly water quality data, in association with the climatic conditions experienced within that year, may ultimately elucidate important information with regards to the correlation between trace elements and heavy metals in water and changing climatic conditions. Overall, it can be concluded that this research was successful, and these practical implications can be applied in future research and water quality investigations worldwide.

5.1 Limitations and Recommendations

There was only one significant limitation encountered in the analysis of water samples for this research, where concentrations of mercury reported in samples collected over all six years of this longitudinal study were shown to be erroneous. In any future research conducted, alternative sample preservation procedures, such as the method suggested by

Louie et al. (2012), or the addition of potassium permanganate and persulfate or gold chloride ($AuCl_3$) to oxidise organo-mercury compounds to the mercuric ion, would be highly recommended for the analysis of elemental mercury in waters. Additionally, other analytical methods/instrumentation may be preferable for the analysis of mercury, such as Cold Vapour Atomic Absorption or Fluorescence Spectrometry (CVAAS or CVAFS), as recommended by the US EPA. Such improvements to methodology to more accurately analyse particular elements of interest may be an important aspect of future work conducted in this area of research.

This research has provided a comprehensive understanding of water quality in the greater Brisbane area with respect to trace element and heavy metal concentrations of various water sources. A more complete understanding of Brisbane municipal water quality could be achieved by investigating additional parameters of water quality. For example, according to the National Health and Medical Research Council (2011), the most acute health effects arise from microbial contamination of waters, indicating the importance of monitoring microbial activity and complying with the microbial guidelines as outlined in the 2011 ADWG. The analysis of phosphates, sulfates and nitrates associated with the decomposition of leaf litter in roof gutters and water tanks, bacterial activity, and contamination from fertilisers would also provide a well-rounded understanding of water quality.

In terms of chemometric analyses, PLS analysis has been shown to be advantageous because it minimises the number of significant variables that require direct analysis. Consequently, future analyses of the trace element and heavy metal content in waters could be conducted with fewer variables, and could therefore be cheaper and faster, while still reaching acceptable levels of understanding. Future work on the PLS model constructed in this research would involve continually adding years of water quality data to the model and refining it in an effort to increase the data variance explained and the predictive ability of the model. Similarly, continuing the analysis of years of water quality data with PROMETHEE and GAIA would allow further investigation into the effects of changing climatic conditions on water quality. Other parameters such as microbial contamination and concentrations of anionic species (phosphates, sulfates and nitrates) may enhance the results achieved with chemometric techniques.

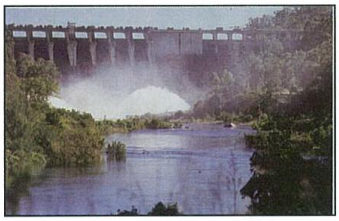
Finally, it would be very interesting to conduct this water quality research in other capital cities within Australia, and to determine where Brisbane's water quality ranks amongst other Australian cities. Such information could be used to optimise water treatment and supply policies throughout the country.

This research encompasses a thorough investigation into the quality of water in the greater Brisbane area in terms of the trace element and heavy metal concentrations found in various water sources. Overall, it can be concluded that the hypothesis for this research, that quantitative ICP-MS data modelled through the use of chemometrics will allow factors including water sources, sources of contaminants and effects of changing climatic conditions to be identified from trace element and heavy metal content of potable Brisbane water, has been fulfilled.

Chapter Six: Appendices

Appendix A (Chapter One): Introduction

SOMERSET DAM
Completed 1959



Somerset Dam - constructed by the Bureau of Industry Stanley River Works Board.

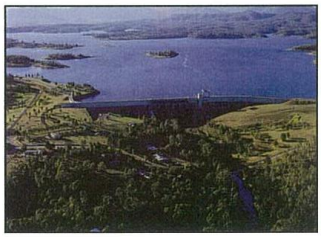
Somerset supplies water to same areas as Wivenhoe Dam.

Catchment Area	1503 sq km
Capacity – Water Supply	380,000 Ml
Capacity – Flood Storage	524,000 Ml
Full Supply Level	99.0 (AHD)*
Submerged Area at Full Supply Level	3,967 ha
Stream Bed Level at Structure	60.4 (AHD)
Spillway Level	100.45 (AHD)
Embankment or Crest Level	107.45 (AHD)
Type of Structure	Concrete 203,000m^3
Length of Wall	305 m
Shoreline	237 km
Spillway Gates	8 of 17.97m x 7.01m
Regulator Valves	4 of 2.3m diameter
Average Evaporation	1,775 mm/year
Average Rainfall	1,230 mm/year
Hydro Electric Station/Dam Structure	4 megawatts
*AHD' – Australian Height Datum	

Figure 6-1. Key features of Somerset Dam (Seqwater, 2013f).
Reprinted from Seqwater Dams: Key Features, Copyright (2013), with permission from Seqwater.

NORTH PINE DAM

Completed in 1976



North Pine Dam was designed by Department of Local Government.

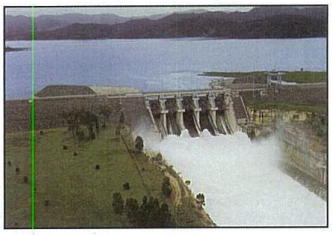
The dam supplies water to Redcliffe, Pine Rivers and Caboolture Shires.

Catchment Area	348 sq km
Capacity – Water Supply	215,000 Ml
Shoreline Area	166 km
Full Supply Level	39.63 (AHD)*
Submerged Area at Full Supply Level	2,121 ha
Stream Bed Level at Structure	4.3 (AHD)
Spillway Level	32.01 (AHD)
Embankment or Crest Level	43.2 (AHD)
Type of Structure	Embankment 275,000m3 Concrete 175,000m^3
Length of Wall	1,375 m
Shoreline	166 km
Spillway Gates	5 of 12.2m x 8.3m
Regulator Valves	2 of 1.4m diameter
Average Evaporation	1,375 mm/year
Average Rainfall	1,175 mm/year
Average Water Supply Yield with 1% risk of depletion	54,750ml/year
*AHD – Australian Height Datum	

Figure 6-2. Key features of North Pine Dam (Seqwater, 2013f).
Reprinted from Seqwater Dams: Key Features, Copyright (2013), with permission from Seqwater.

WIVENHOE DAM

Completed 1985



Wivenhoe Dam -constructed by the Water Resources Commission.

Wivenhoe supplies water to the cities of Brisbane, Ipswich, Logan, Gold Coast and Shires of Beaudesert, Esk, Gatton, Laidley, Kilcoy & Nanango plus Tarong and CS Energy.

Catchment Area	5,554 sq km
Capacity – Water Supply	1,165,000 Ml
Capacity – Flood Storage with upgrade to Spillway	2,000,000 Ml
Shoreline Area	462 km
Full Supply Level	67.0 (AHD)*
Submerged Area at Full Supply Level	10,940 ha
Stream Bed Level at Structure	23.0 (AHD)
Spillway Level	57.0 (AHD)
Embankment or Crest Level	79.0 (AHD)
Type of Structure	Embankment 4 million m^3 Concrete 140,000m^3
Length of Wall	2,300 m
Spillway Gates	5 of 12.0m x 16.6m
Regulator Valves	1 of 1.5m diameter
Average Evaporation	1,872 mm/year
Average Rainfall	940 mm/year
Hydro Electric Station/Dam Structure	4.5 megawatts
*AHD – Australian Height Datum	

Figure 6-3. Key features of Wivenhoe Dam (Seqwater, 2013f).
Reprinted from Seqwater Dams: Key Features, Copyright (2013), with permission from Seqwater.

Appendix B (Chapter Three): Research Design and Methodology

Table 6-1. The volumes of the Agilent Standard solutions required for each concentration of the calibration standard solutions and the internal standard solution.

Dilution	Blank	1-to-20,000 (Std 1)	1-to-10,000 (Std 2)	1-to-1000 (Std 3)	1-to-100 (Std 4)
Agilent Environmental Calibration Standard (#5183-4688)	0 µL	12.5 µL	25 µL	250 µL	2500 µL ≈2.5 mL
Single Element Standard – Mercury (#8500-6941)	0 µL	12.5 µL	25 µL	250 µL	2500 µL ≈2.5 mL
For microelements: **10 mg/L** of Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn, Th and U; and Hg.	Blank	0.5 µg/L	1 µg/L	10 µg/L	100 µg/L
For macroelements: **1000 mg/L** of Fe, K, Ca, Na and Mg.	Blank	50 µg/L	100 µg/L	1000 µg/L	10,000 µg/L
Agilent Internal Standard Mixture (#5188-6525) **10 mg/L** of ^{6}Li, Sc, Ge, Y, In, Tb and Bi	40 µL	40 µL	40 µL	40 µL	40 µL
Internal Standard Concentration	10 µg/L	10 µg/L	10 µg/L	10 µg/L	10 µg/L

P/A Factor Tuning Report

Acquired:Jun 14 2013 11:47 am

Mass[amu]	Element	P/A Factor
23	Na	0.071677
24	Mg	0.071954
27	Al	0.073004
51	V	0.075836
53	Cr	0.077096
55	Mn	0.079724
59	Co	0.077839
60	Ni	0.078562
63	Cu	0.078921
66	Zn	0.078766
75	As	0.078567
88	Sr	0.078073
89	Y	0.077976
111	Cd	0.079035
115	In	0.079623
137	Ba	0.081824
172	Yb	0.092801
205	Tl	0.080856
206	(Pb)	0.080433
207	(Pb)	0.080393
208	Pb	0.083793
209	Bi	0.079287
238	U	0.079644

===Detector Parameters===

Discriminator: 8.0 mV

Analog HV: 2050 V

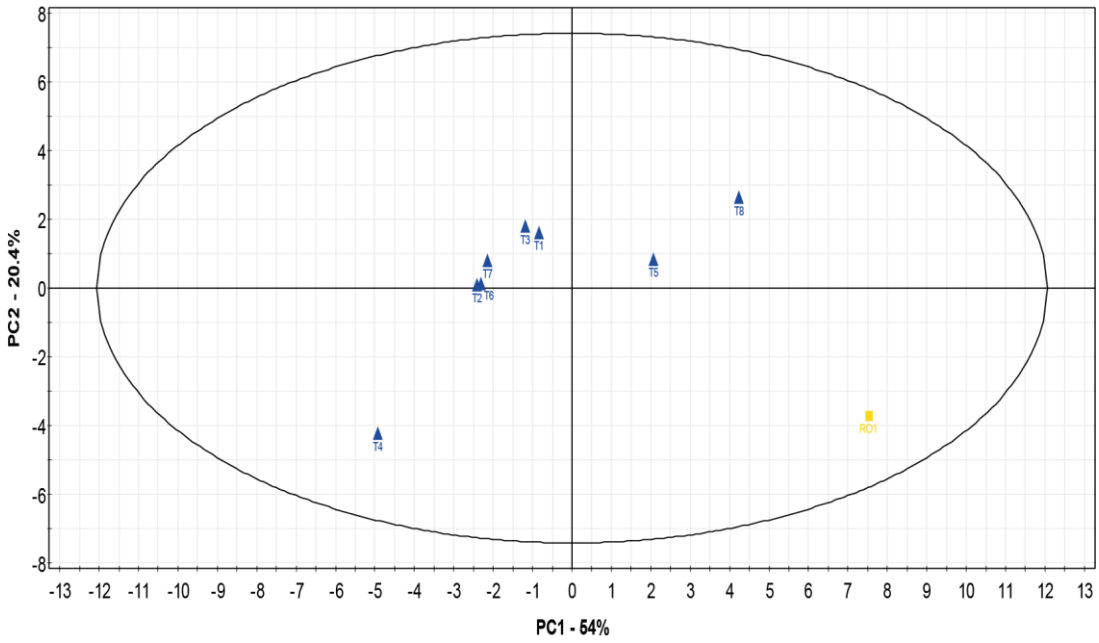
Pulse HV: 1240 V

Figure 6-4. P/A Factor Tuning Report for Detector Parameters set for 2013 ICP-MS analysis in this research.

Appendix C (Chapter Four): Results and Discussion

C-1 Batch by Batch Chemometric Analysis of Historical Data

2008 Batch #1 – 08C07



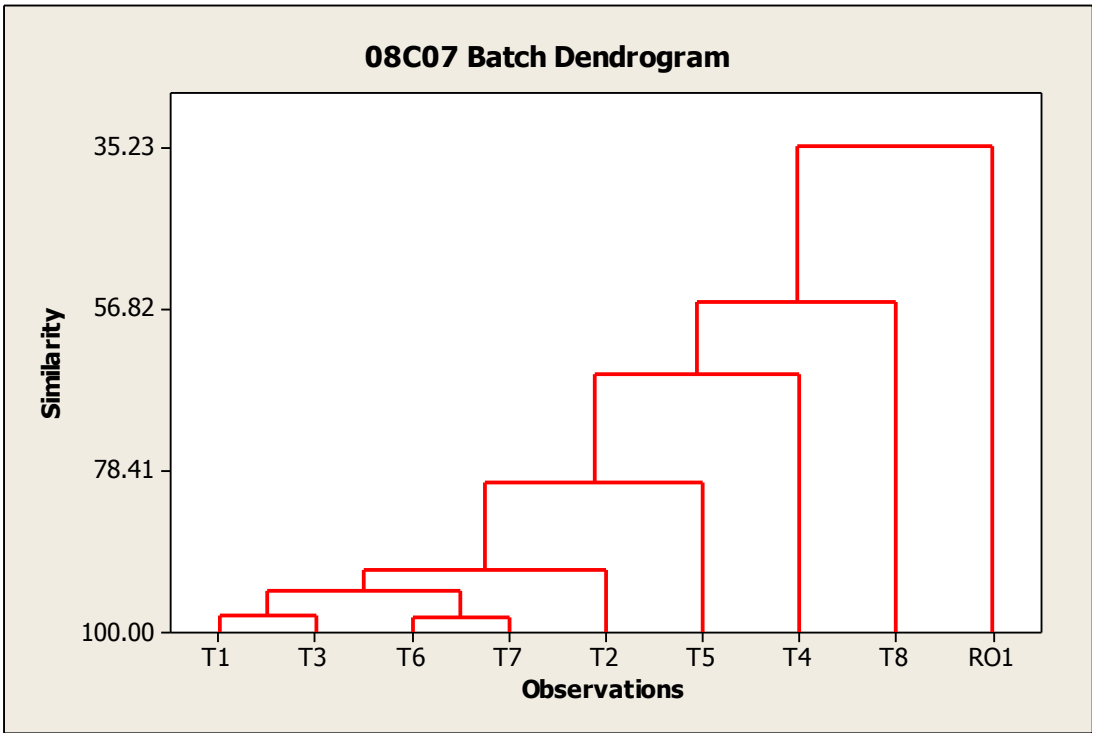
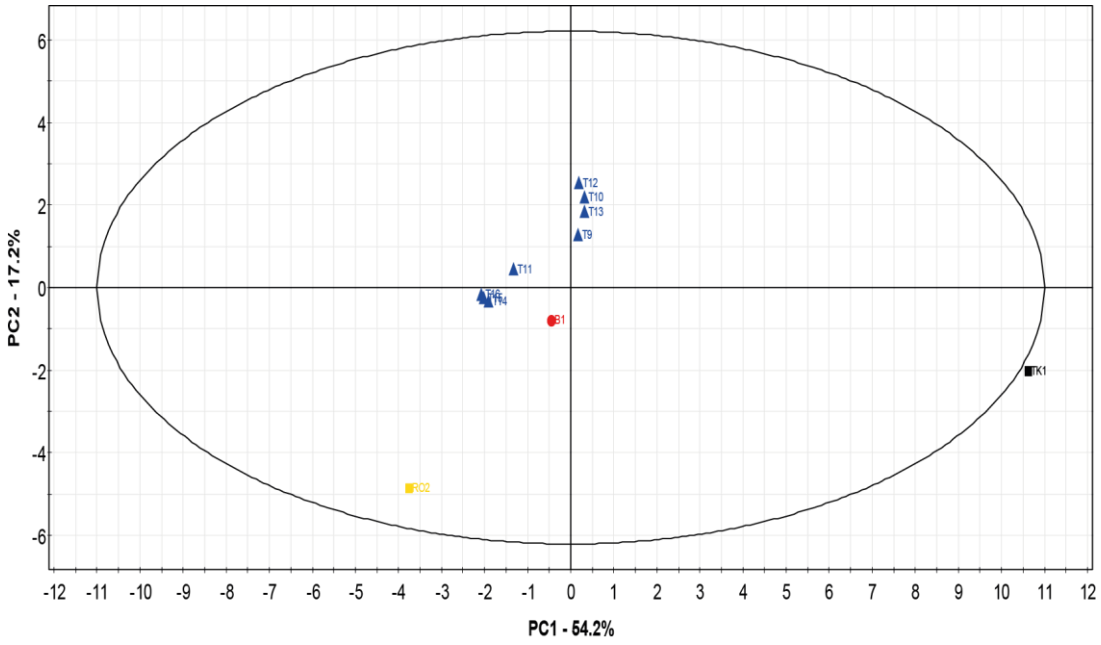


Figure 6-5. PCA scores plot and HCA dendrogram displaying data from batch 08C07. Both show the reverse osmosis sample clearly separate from the tap water samples investigated in this batch.

2008 Batch #2 – 08C11



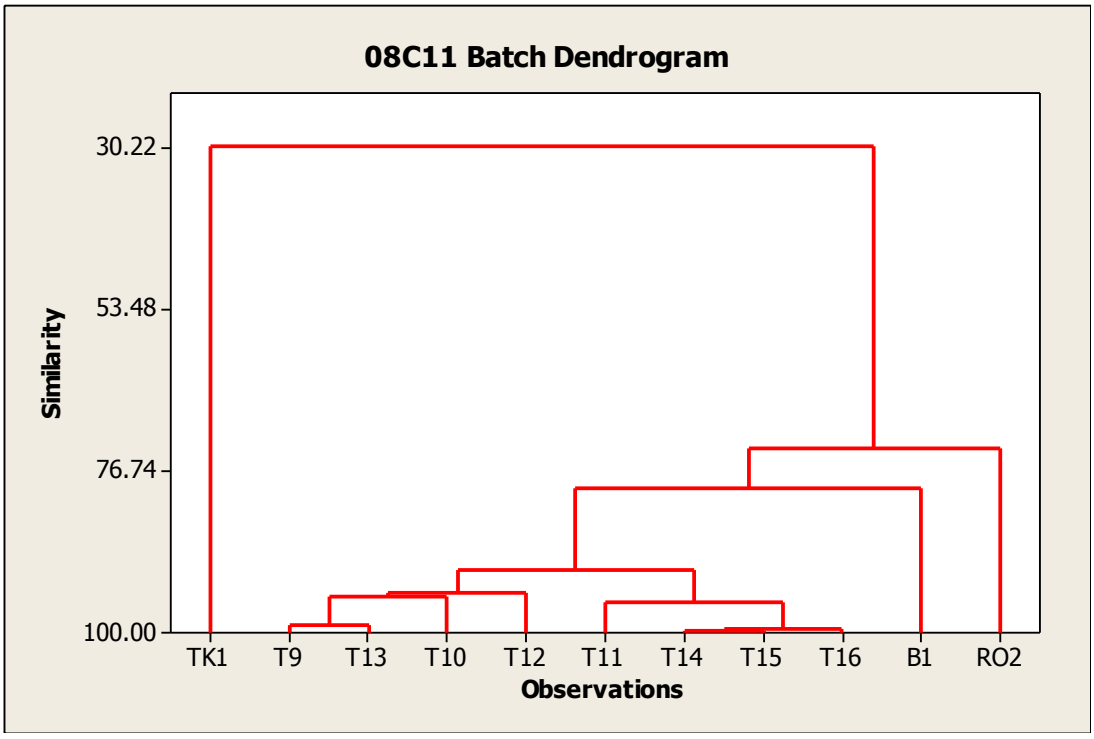
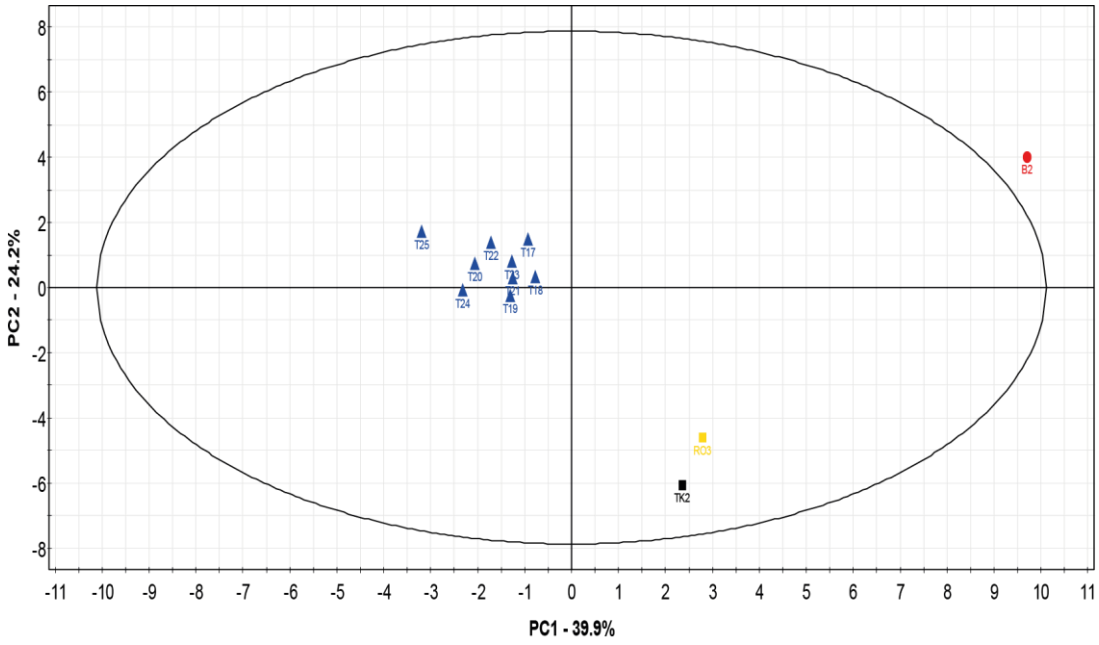


Figure 6-6. Matching PCA scores plot and HCA dendrogram for batch 08C11. All different water samples cluster accordingly: the tank water sample is the greatest distance from the tap water samples, followed by the reverse osmosis sample; finally, the bottled water sample is the closest to the tap water samples collected.

2008 Batch #3 – 08C14



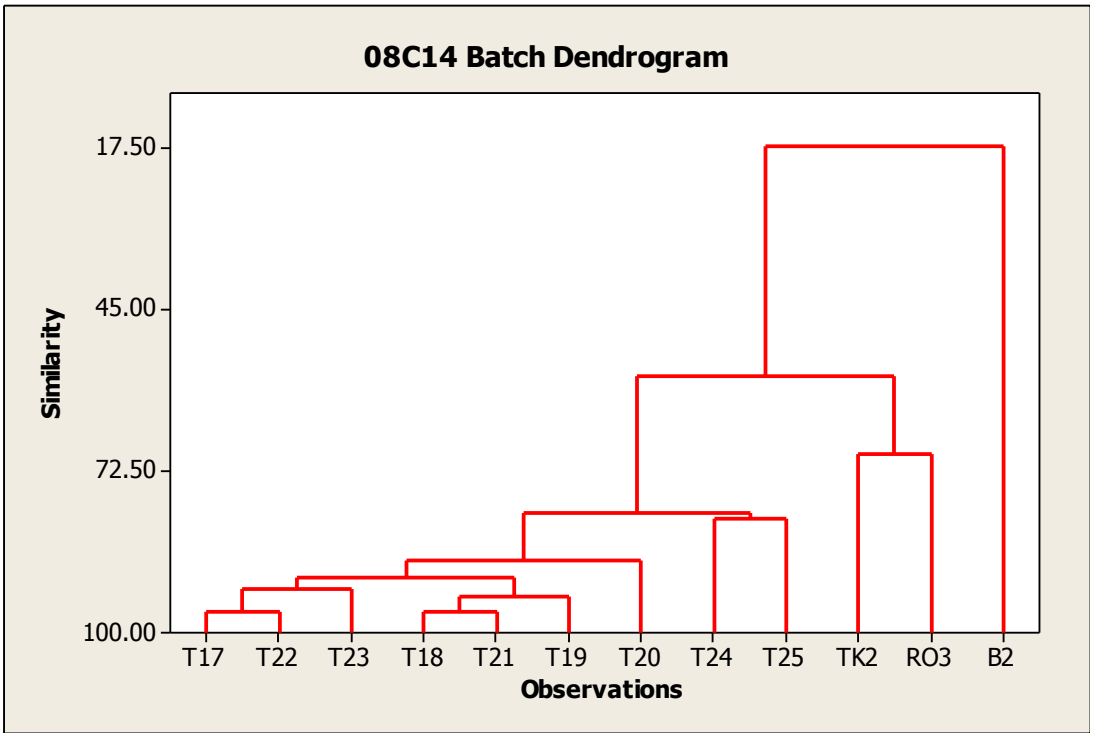
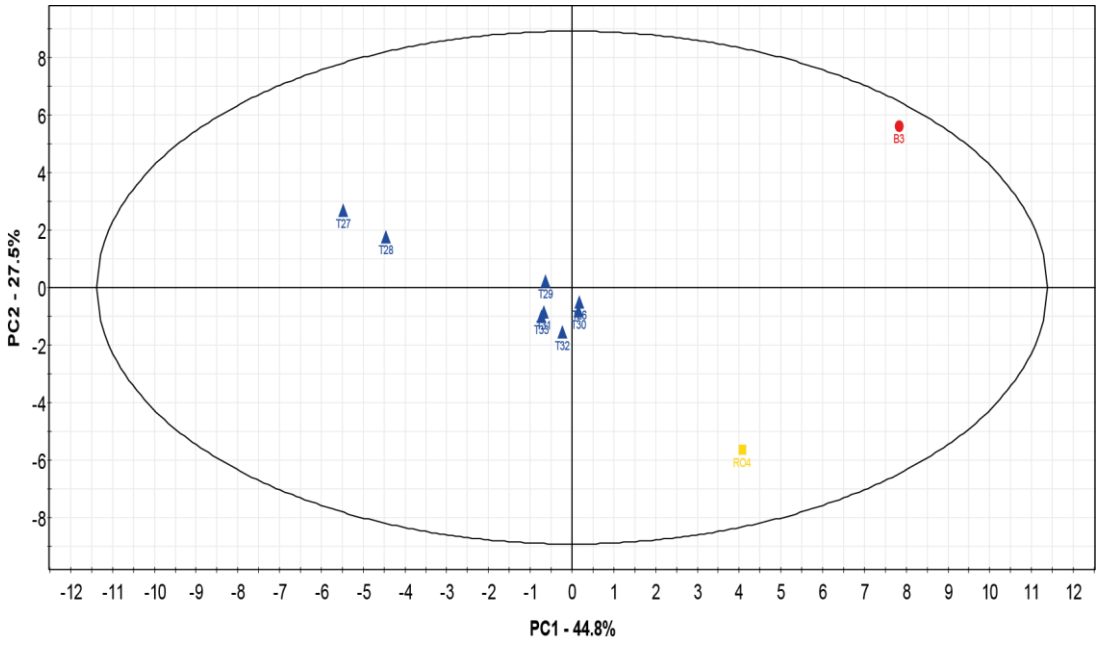


Figure 6-7. The tank and reverse osmosis water samples are clustered in both the PCA scores plot and the HCA dendrogram. The bottled water sample is a significant distance from the tap water samples, and this is reflected in both plots – in fact, in the PCA scores plot, the bottled water sample lies outside the Hotelling T2 95% confidence ellipse, and so may be classed as an outlier in batch 08C14.

2008 Batch #4 – 08C18



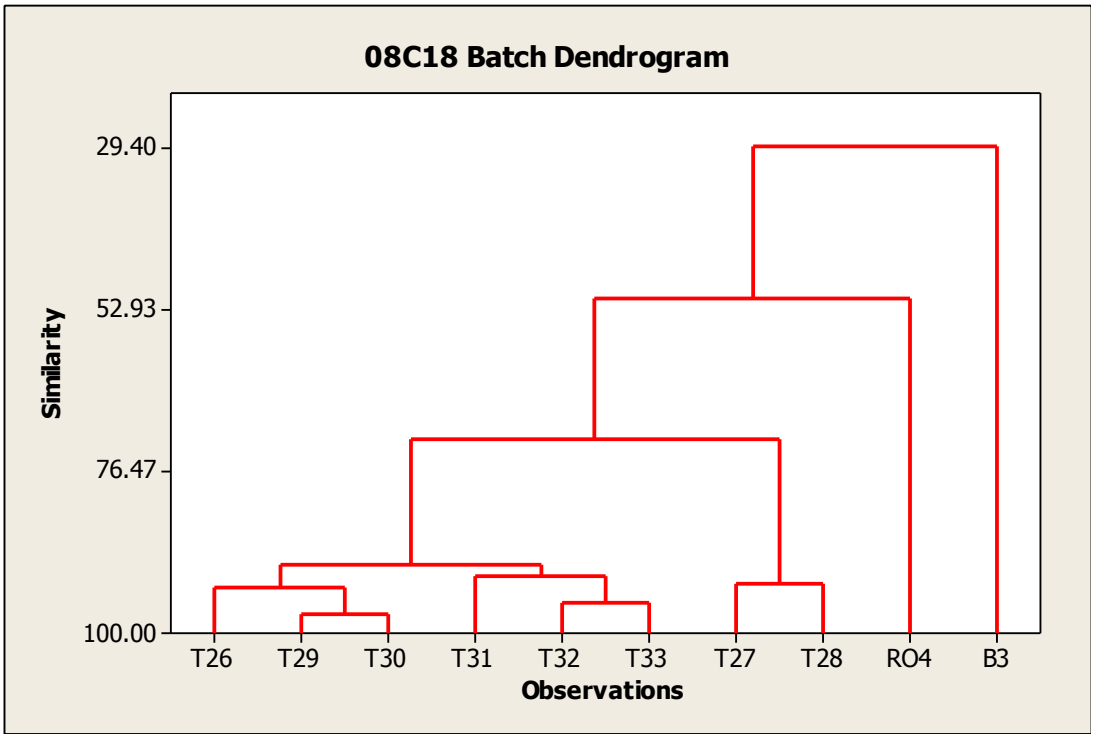
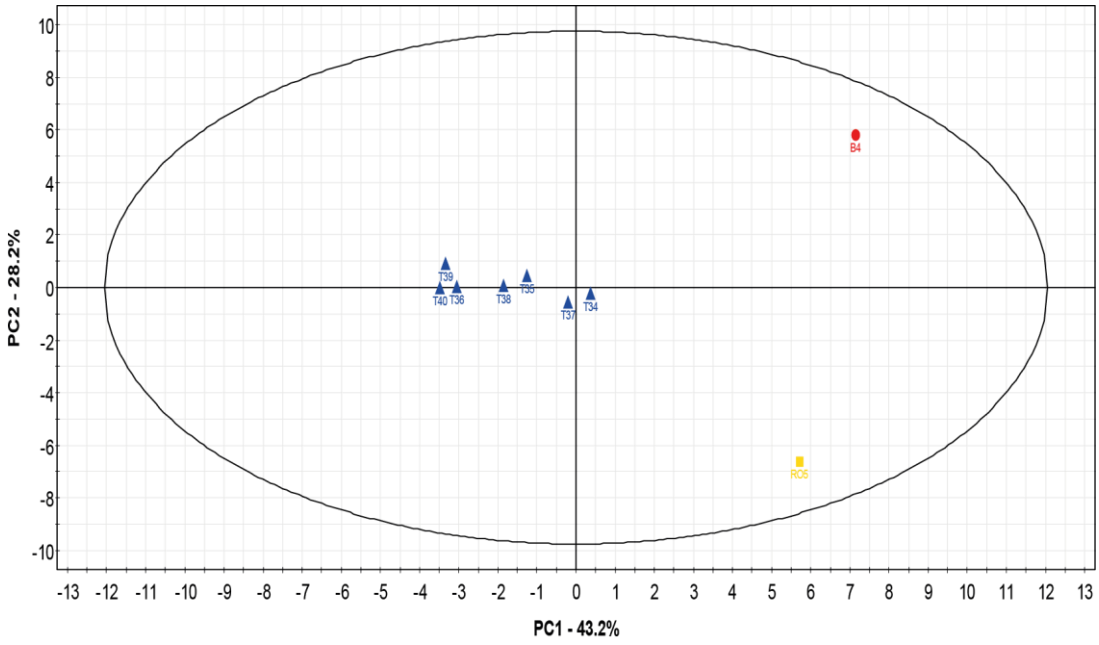


Figure 6-8. PCA scores plot and HCA dendrogram for batch 08C18 showing the bottled water sample the greatest distance from and therefore least similar to the cluster of tap water samples; the reverse osmosis sample is also clustered separately.

2008 Batch #5 – 08D01



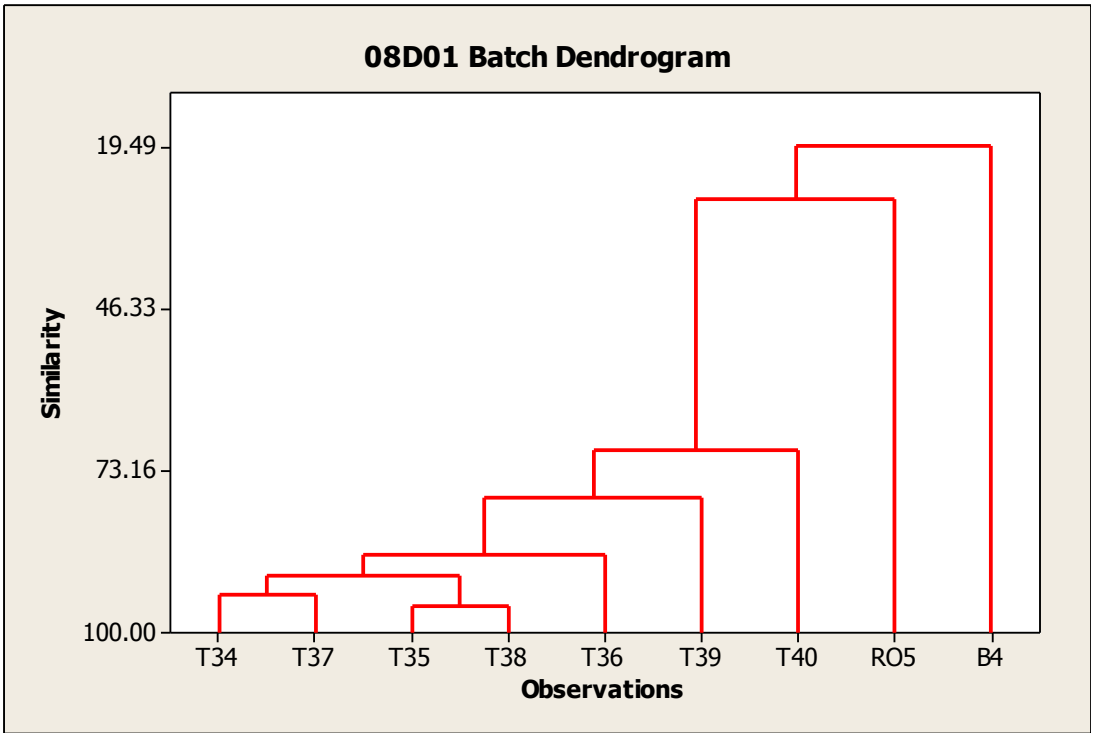
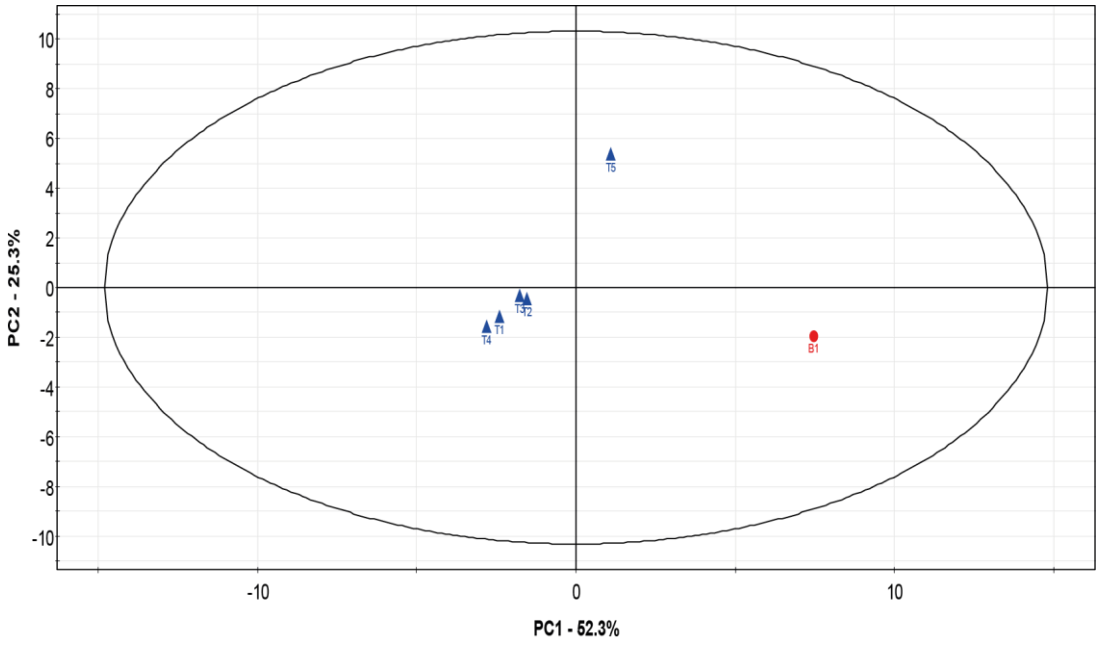


Figure 6-9. PCA scores plot and HCA dendrogram for batch 08D01 distinctly showing the bottled and reverse osmosis water samples as separate from the central cluster of tap water samples.

2009 Batch #1 – 09C03



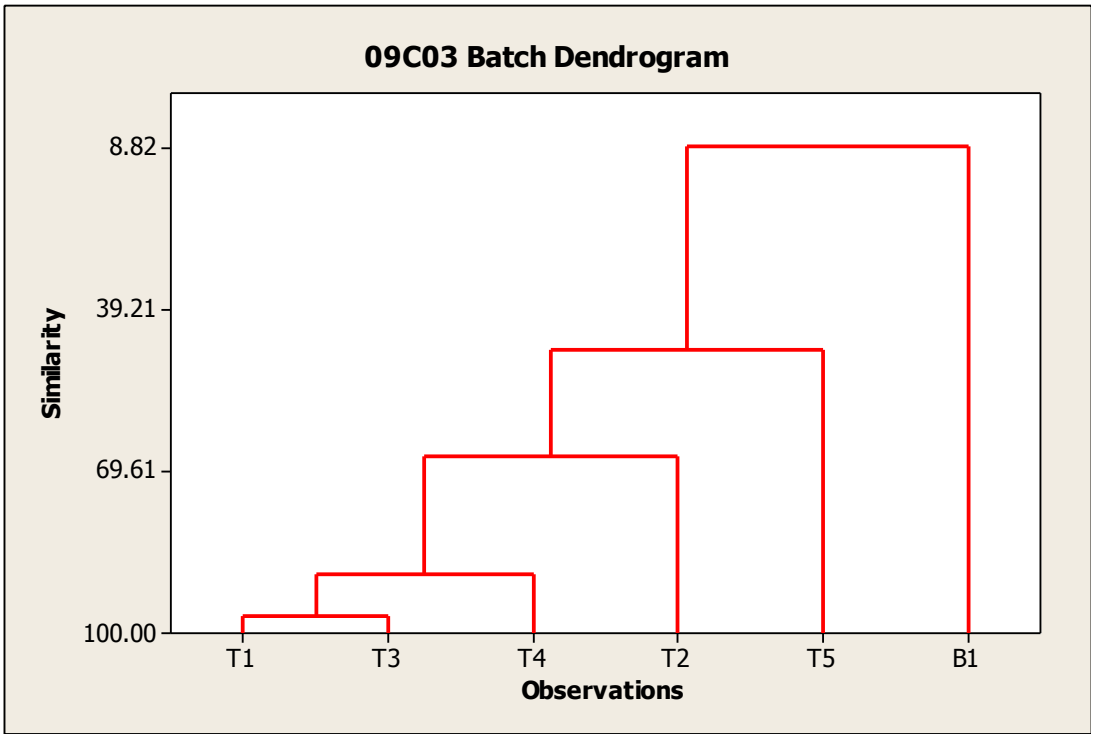
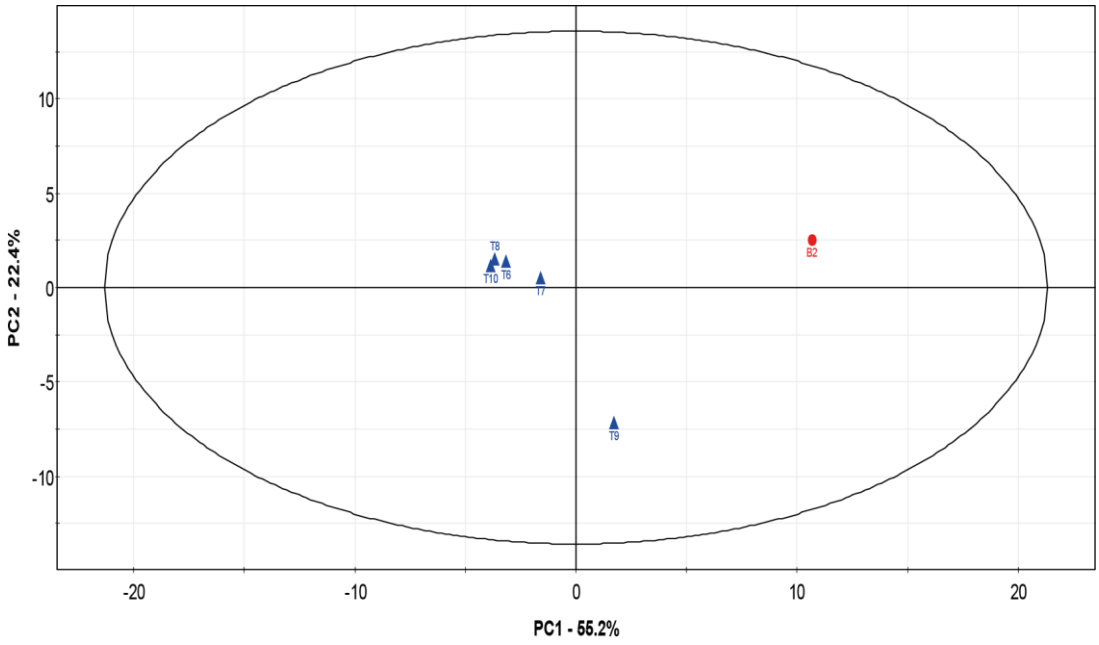


Figure 6-10. Batch 09C03 simply contained tap water samples and a single bottled water sample (brand: Perrier). The PCA scores plot and HCA dendrogram both show the separation of the bottled water from the remaining tap water samples.

2009 Batch #2 – 09C06



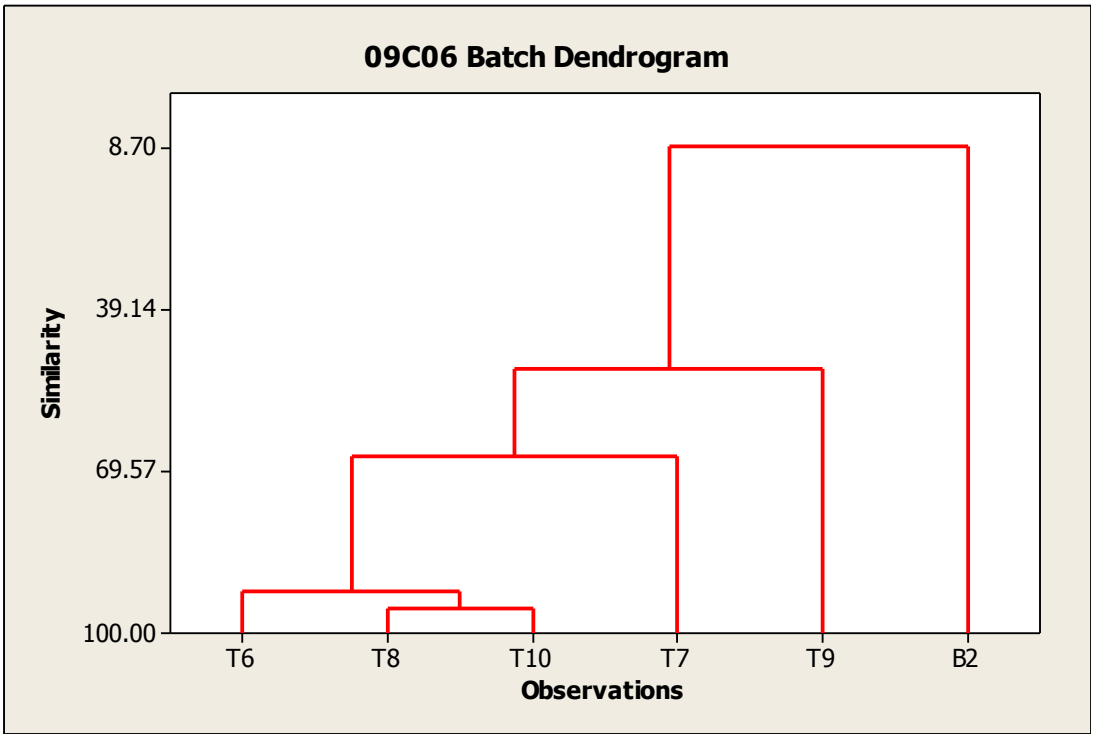
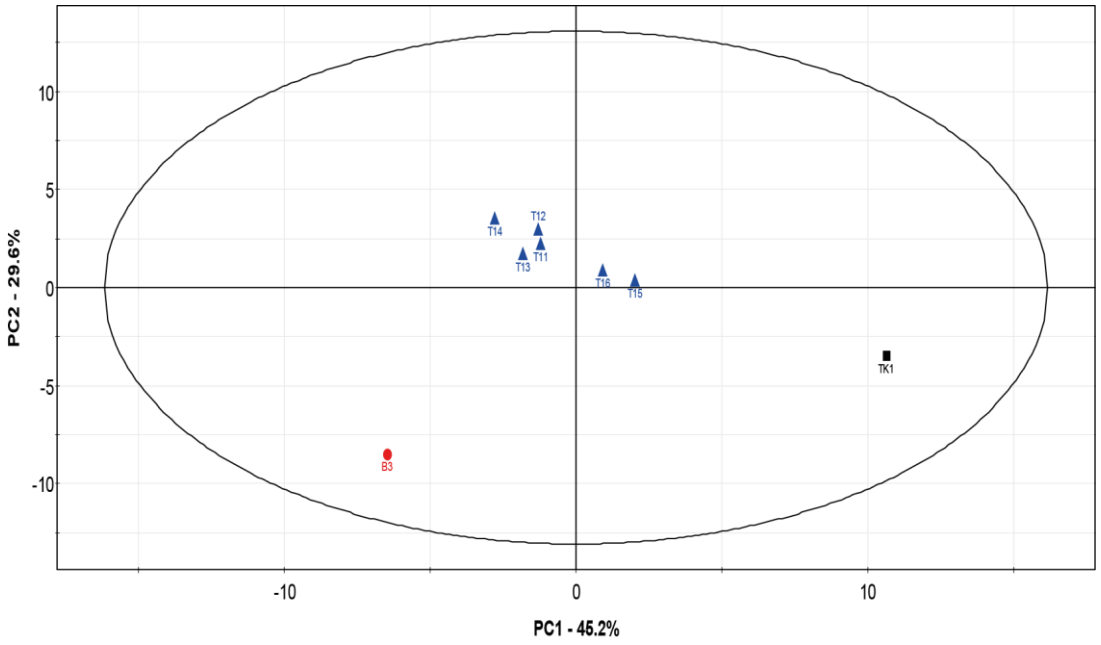


Figure 6-11. PCA scores plot and HCA dendrogram for batch 09C06 demonstrating the relationship between the bottled water sample and the tap water samples. The PCA scores plot also shows the significant distance between tap water sample T9 and the main tap water cluster. It may be inferred that this difference is because sample T9 was collected from the Gold Coast, whereas the remaining samples were collected in the greater Brisbane area.

2009 Batch #3 – 09C10



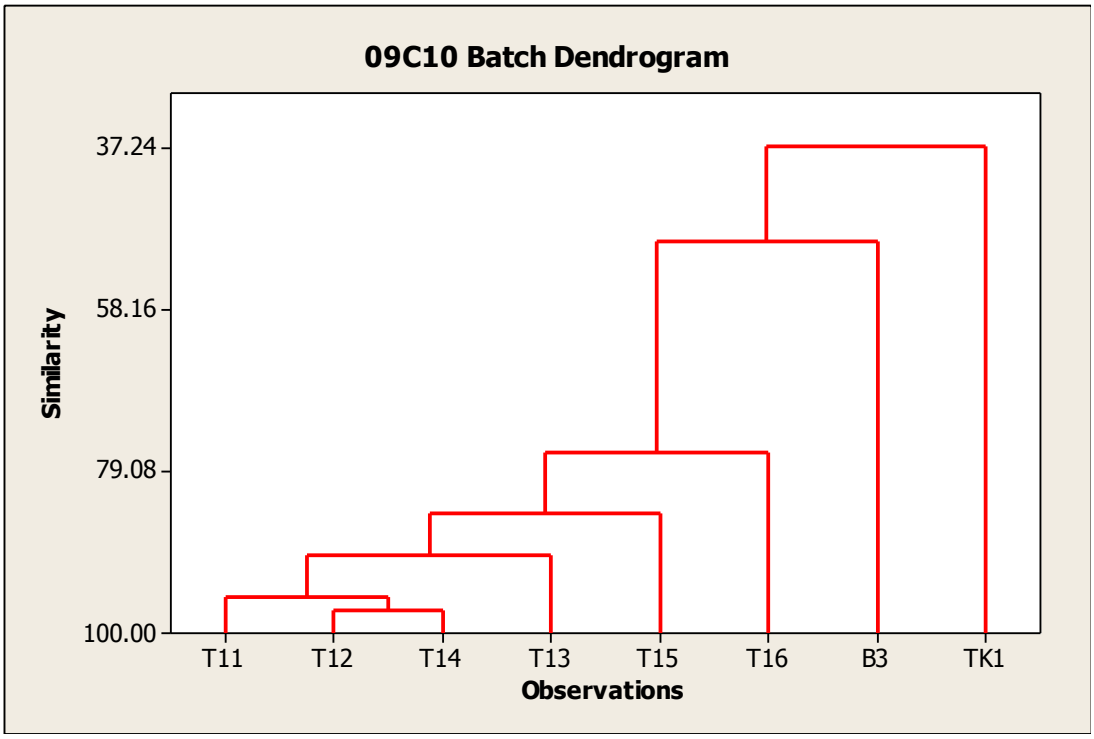
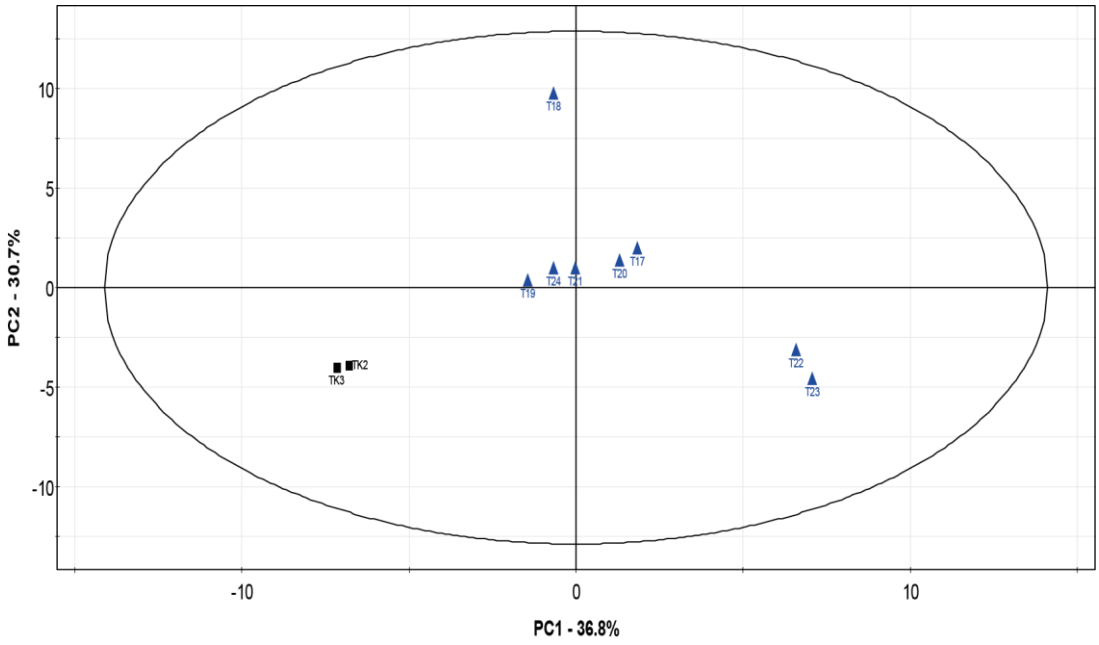


Figure 6-12. PCA scores plot and HCA dendrogram for batch 09C10 both show the tank and bottled water samples similar distances from the cluster of tap water samples; therefore, it is clear that both of these samples are indeed different from tap water.

2009 Batch #4 – 09C17



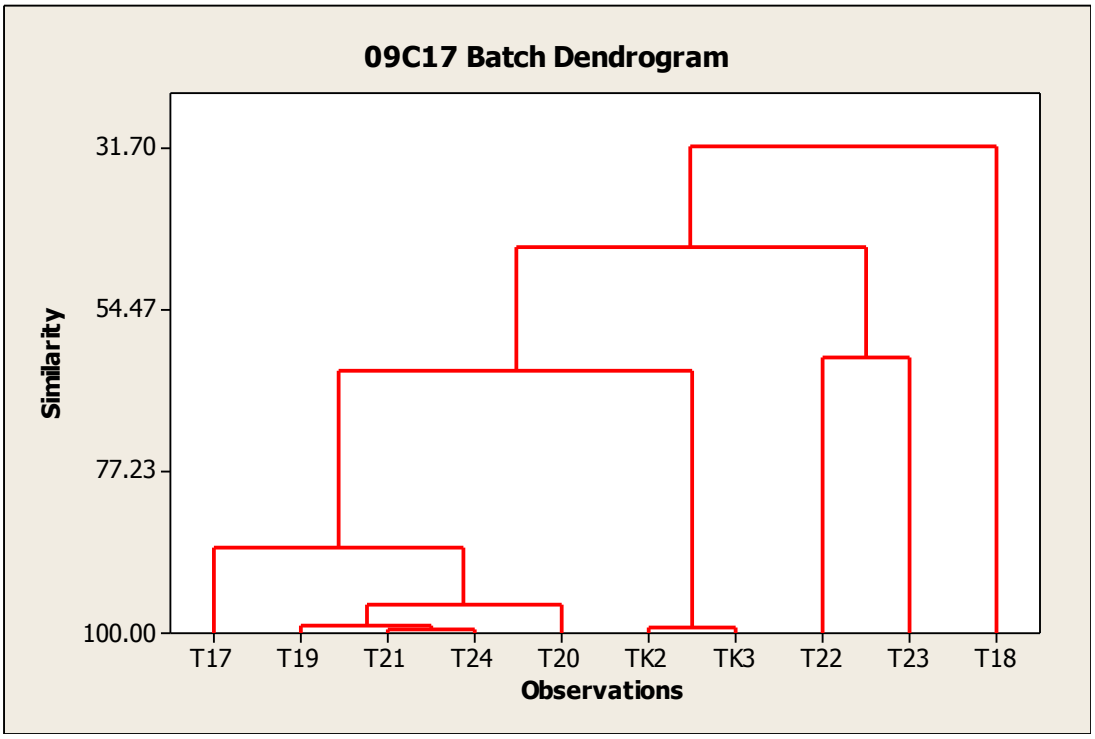
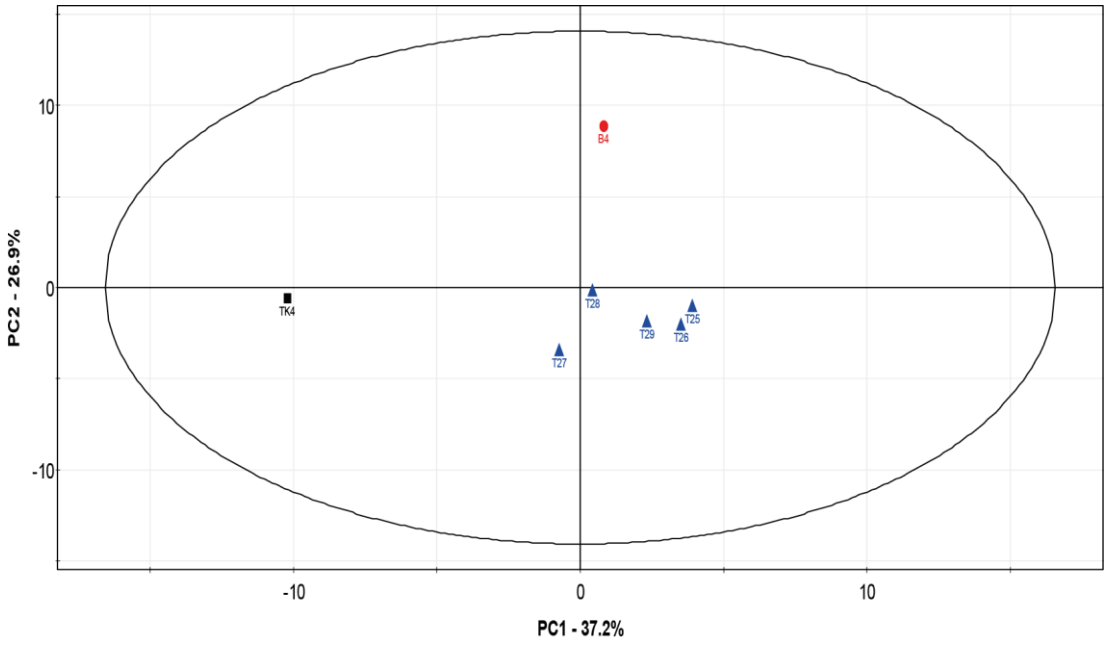


Figure 6-13. The two tank water samples clearly clustered in both the PCA scores plot and the HCA dendrogram for batch 09C17 were collected from the same tank, where one sample was filtered and the other was not. The relationship between the waters from the same tank is apparent, and it can be inferred that there is a detectable difference between a filtered and non-filtered water sample.

2009 Batch #5 – 514Fri



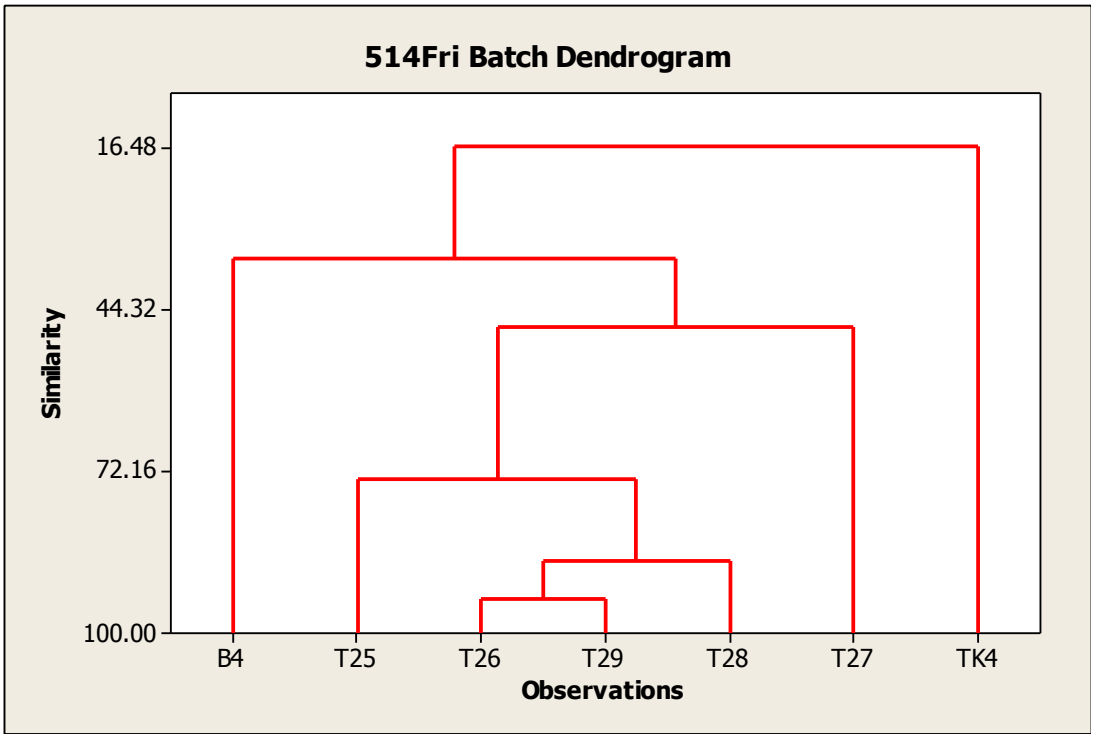
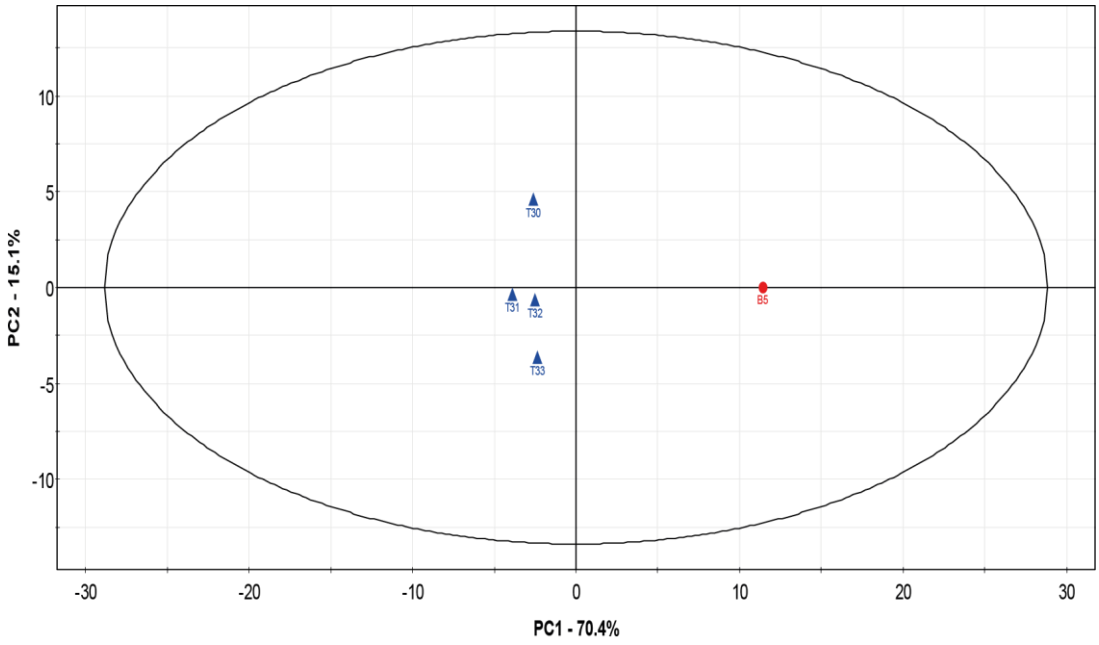


Figure 6-14. PCA scores plot and HCA dendrogram both showing the distinction of the tank and bottled water samples from the tap water samples in batch 514Fri.

2009 Batch #6 – PQB514



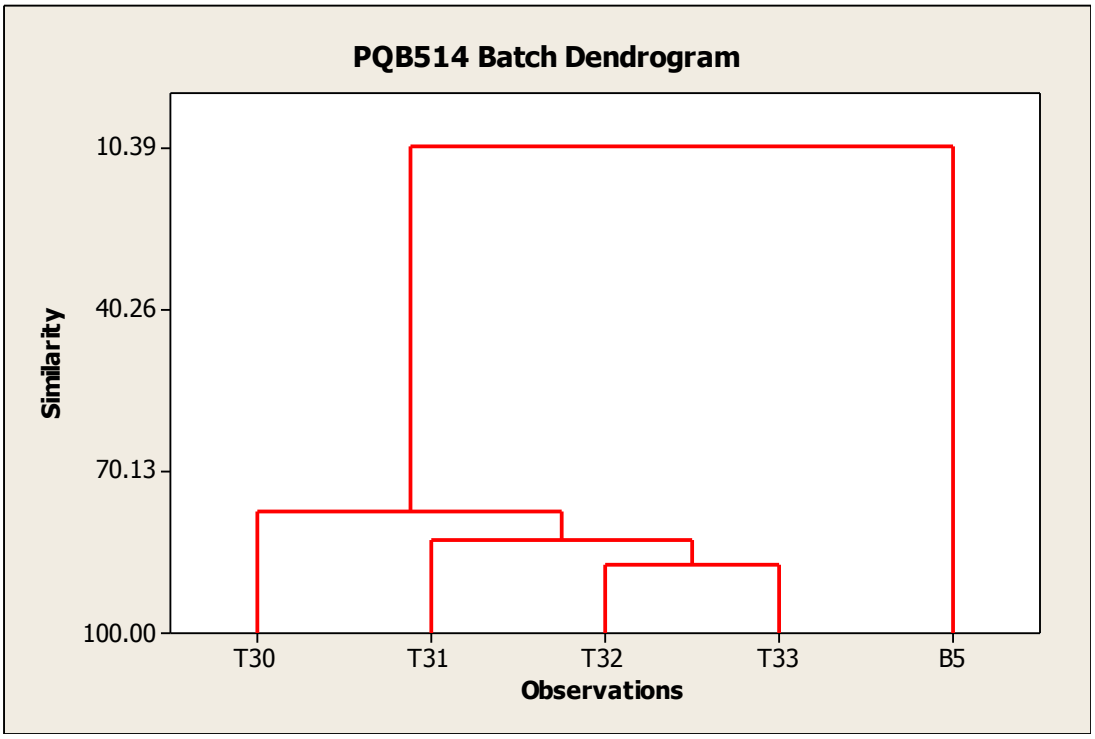
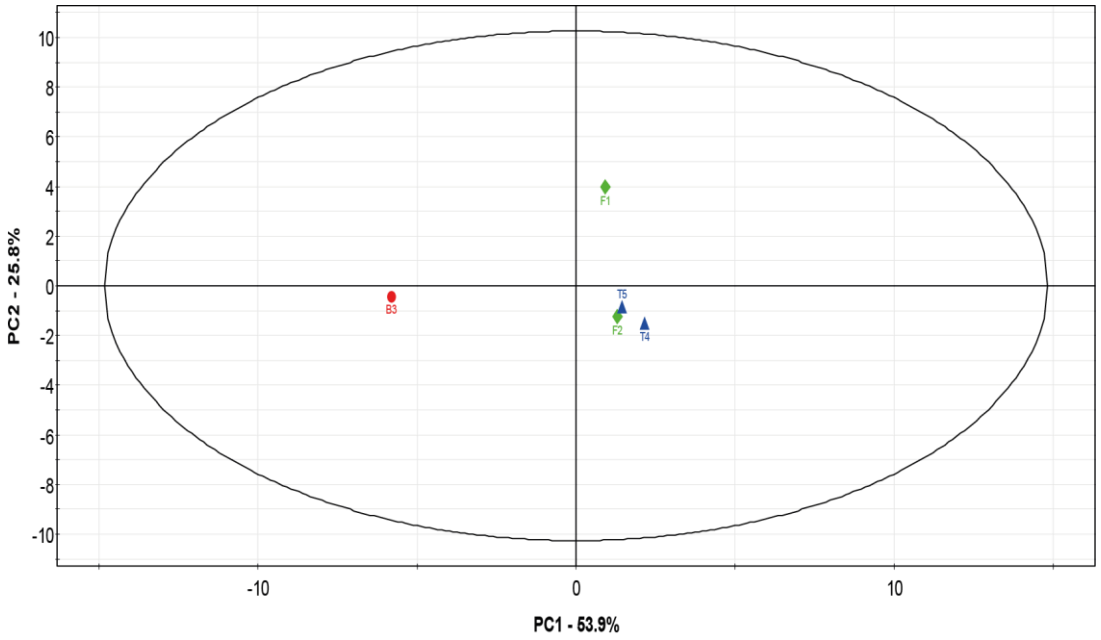


Figure 6-15. The separation of the bottled water sample from the tap water samples collected in the small PQB514 batch is very obvious on the PCA scores plot and the HCA dendrogram shown here.

2010 Batch #2 – 10D30



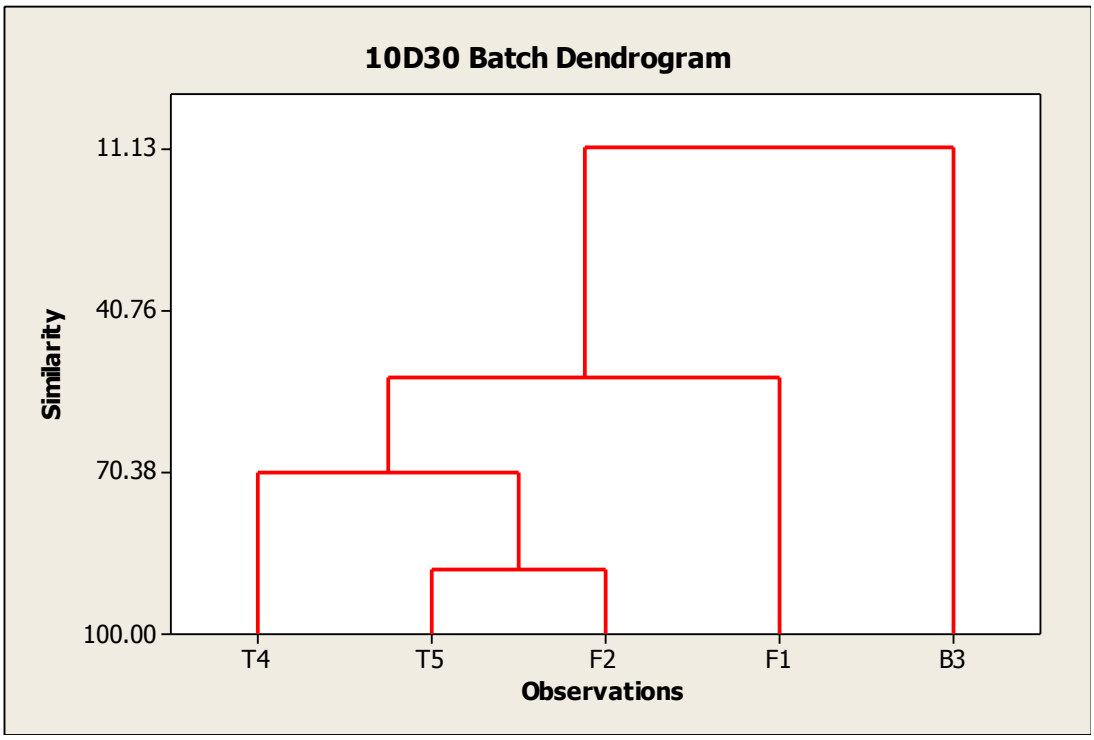
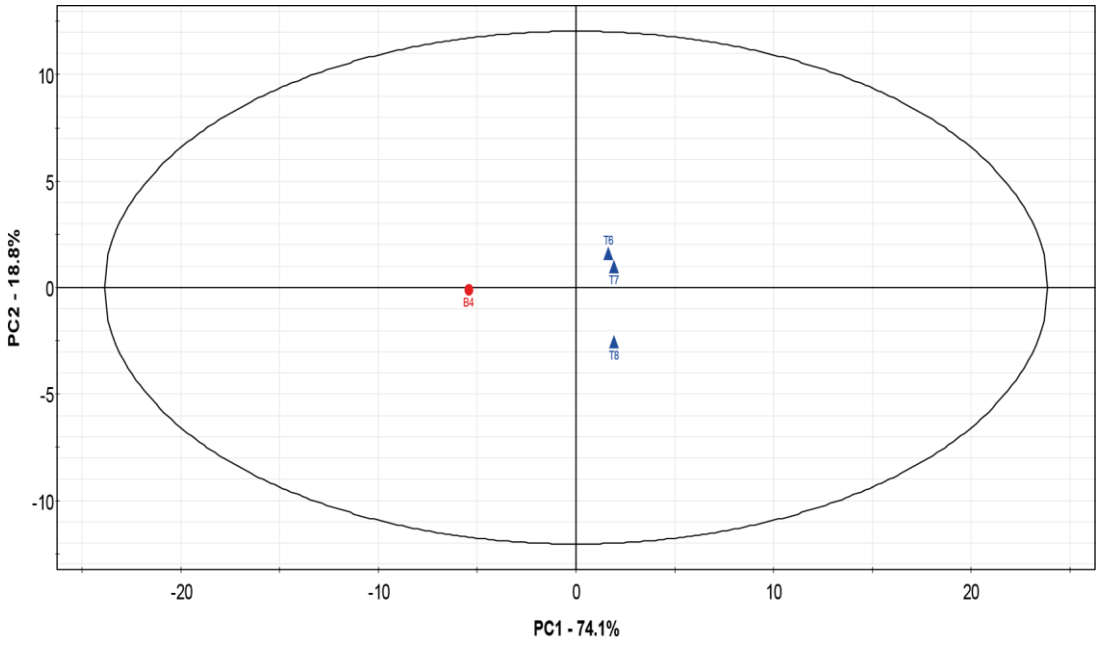


Figure 6-16. The relationship between tap water and filtered water samples collected from the same household in Bray Park (samples T5 and F2) is made obvious on the PCA scores plot and HCA dendrogram. The remaining tap and filtered water samples were collected from different suburbs and so are not related, while the bottled water sample is distinctly separate from all other samples in batch 10D30.

2010 Batch #3 – 10E11



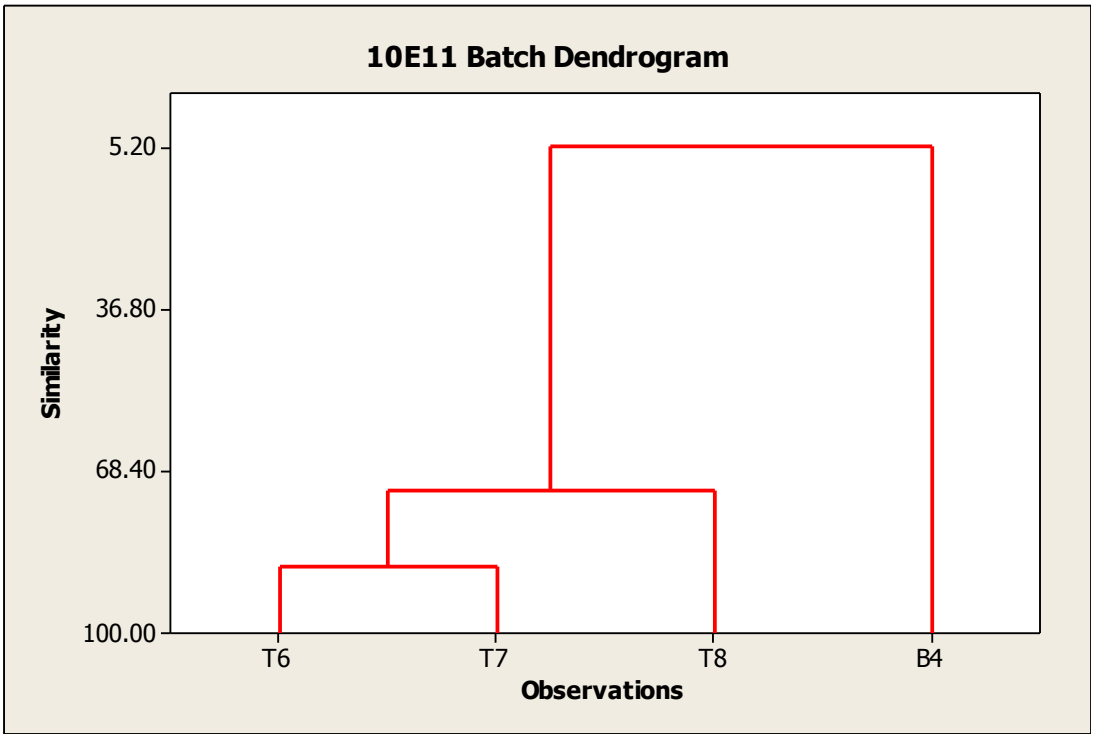
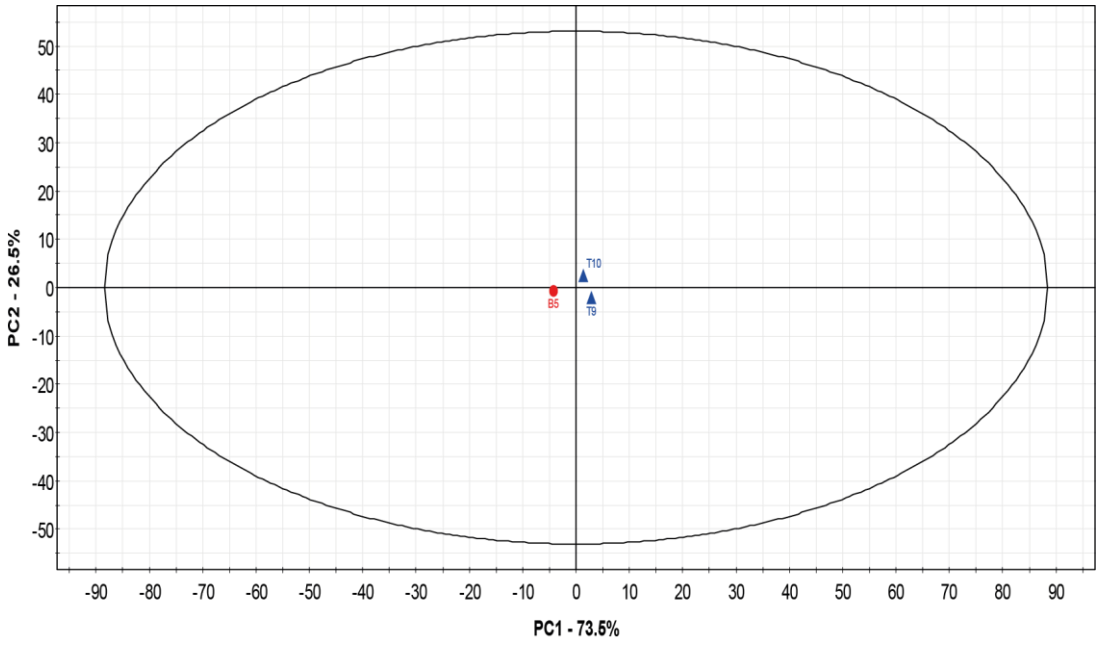


Figure 6-17. The PCA scores plot and HCA dendrogram for the small 10E11 batch simply shows the separation of the bottled water sample from the tap water samples in this analysis.

2010 Batch #4 – 10E14



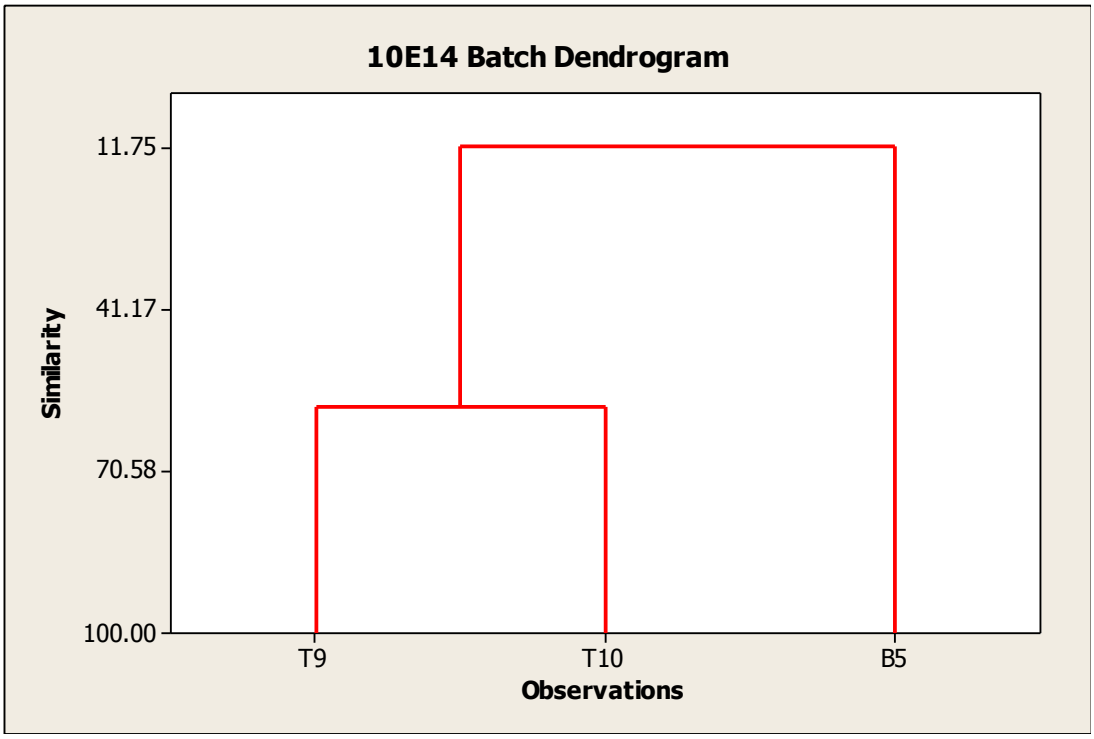
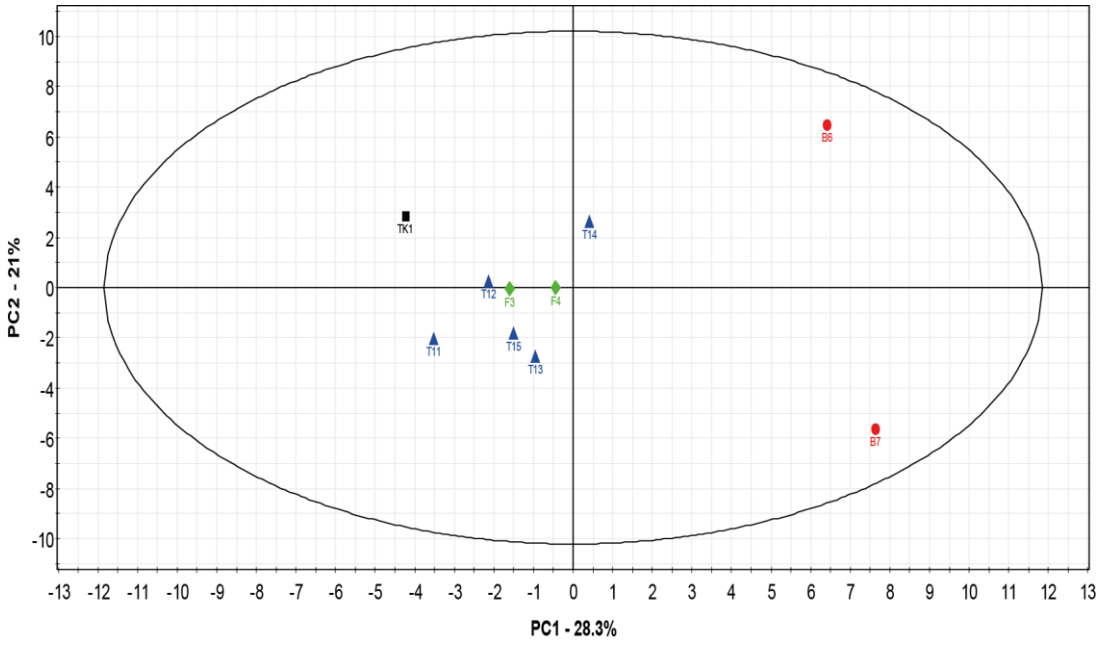


Figure 6-18. PCA scores plot and HCA dendrogram showing the bottled water sample as distinct from the two tap water samples tested in batch 10E14.

2010 Batch #5 – 513Fri10



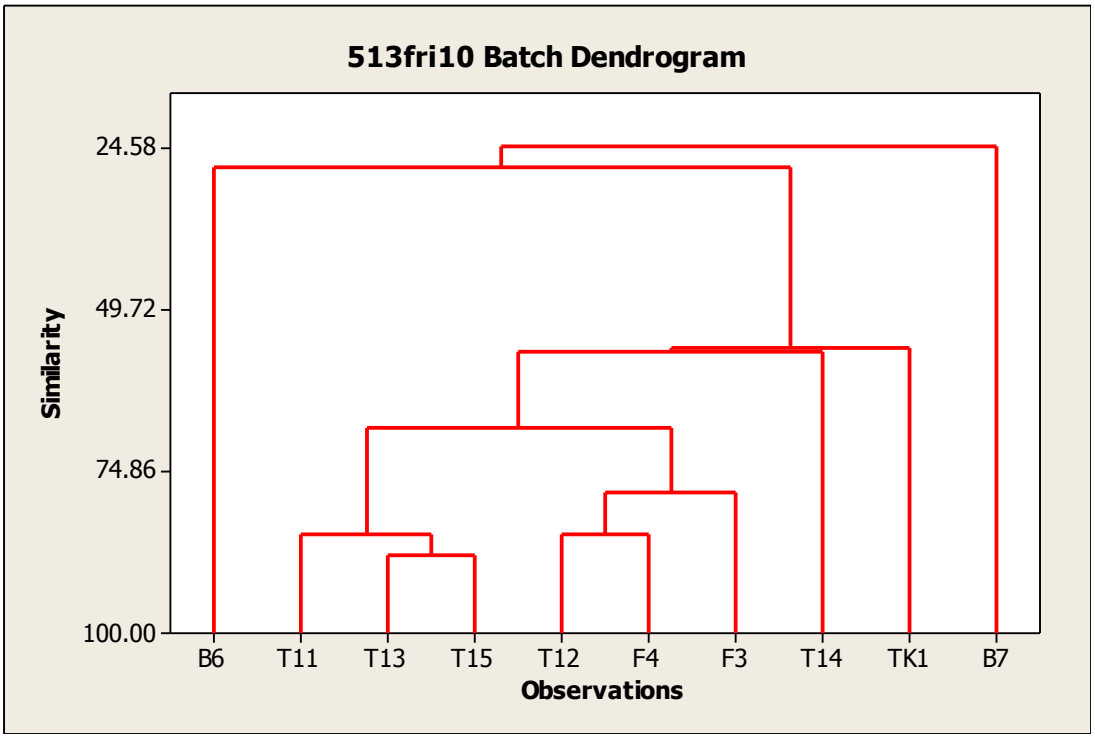
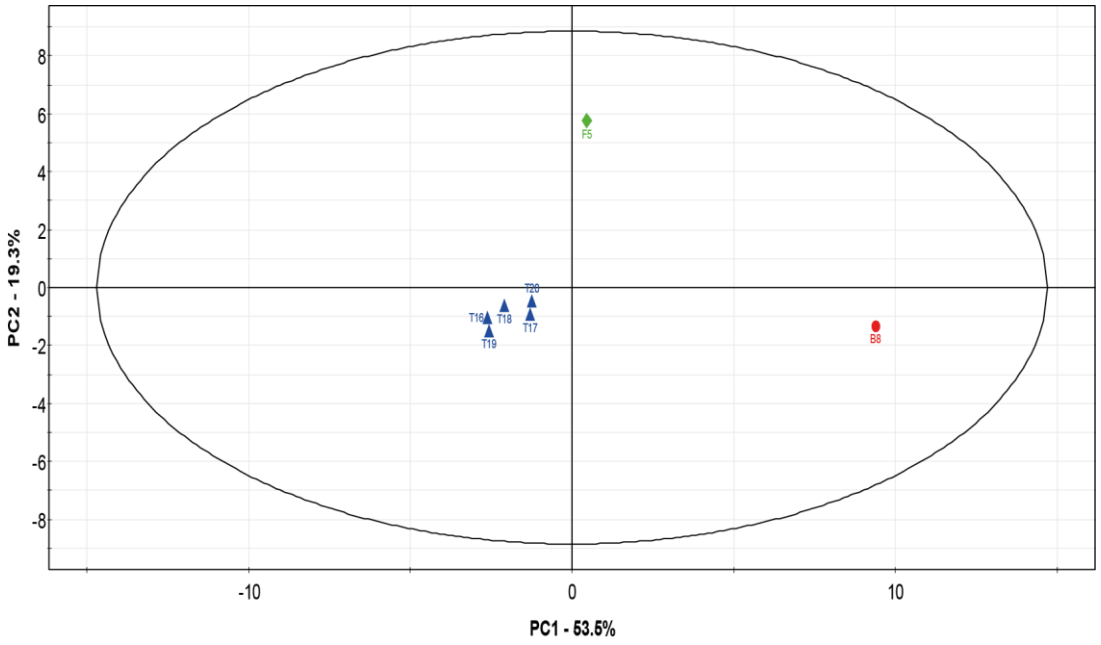


Figure 6-19. The PCA scores plot for batch 513fri10 shows both bottled water brands, Fiji and evian®, to one side and almost equal distance from the remaining water samples investigated here. This is confirmed by the HCA dendrogram, where these samples are separate from the tap and filtered water cluster. The HCA dendrogram also displays a close relationship between between tap water sample T12, and the two filtered water samples, F4 and F3. Samples T12 and F3 were collected from the same suburb/area and are included in the same cluster; however, F4 was from a different suburb. In this case, it may be inferred that both sample type (filtered) and location are significant factors for the clustering of these samples.

2010 Batch #6 – 513T134



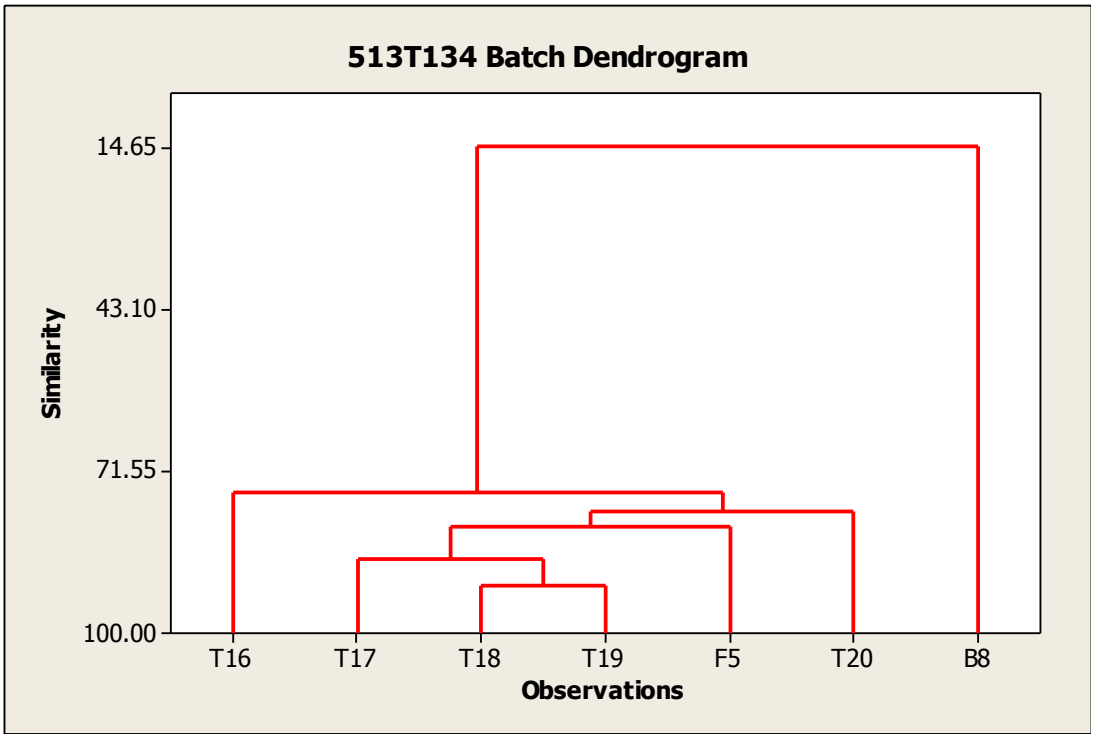
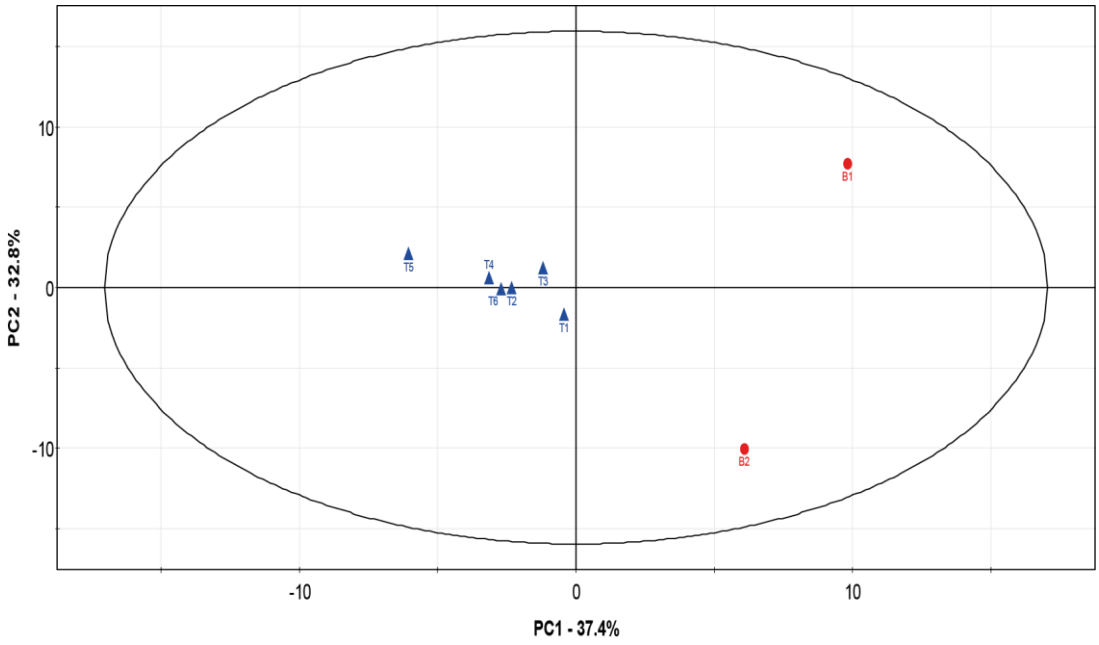


Figure 6-20. PCA scores plot and HCA dendrogram for batch 513T134 clearly demonstrate the separation of the bottled water sample from the tap water cluster. The filtered water sample is distinguished from the tap water cluster on the PCA scores plot, while the HCA dendrogram demonstrates that it is similar to the tap water samples collected. This is believed to be because this filtered water sample and several of the tap water samples were all collected from locations within QUT Gardens Point.

2011 Batch #1 – 11E20



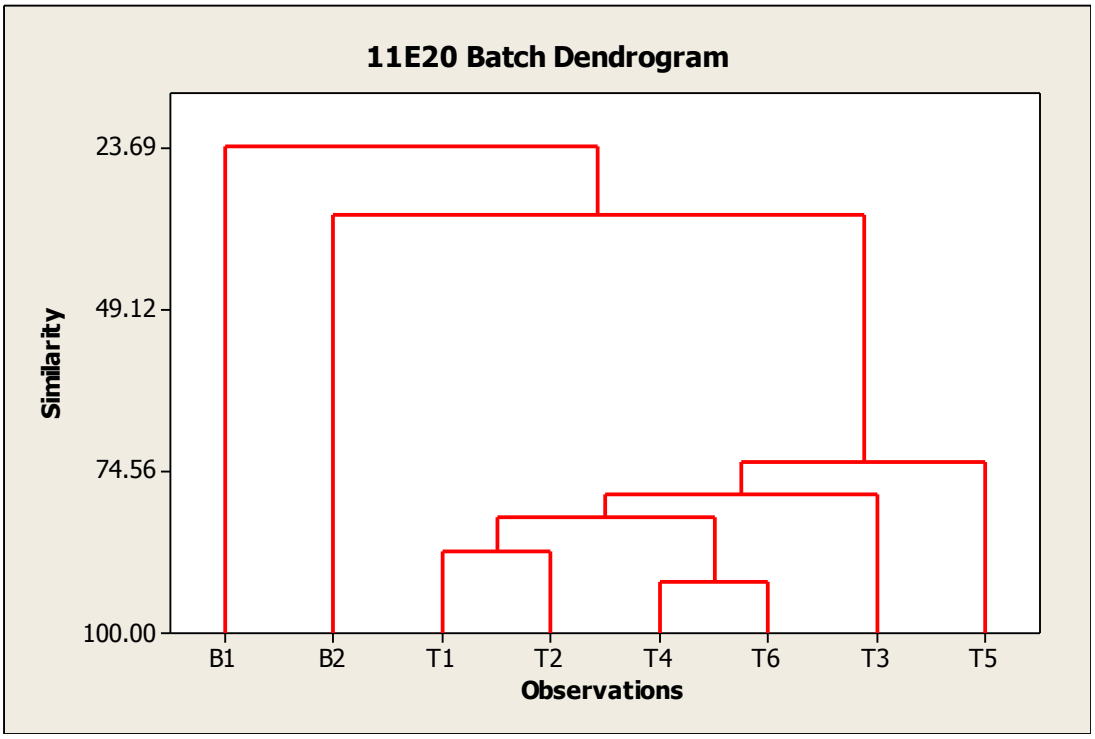
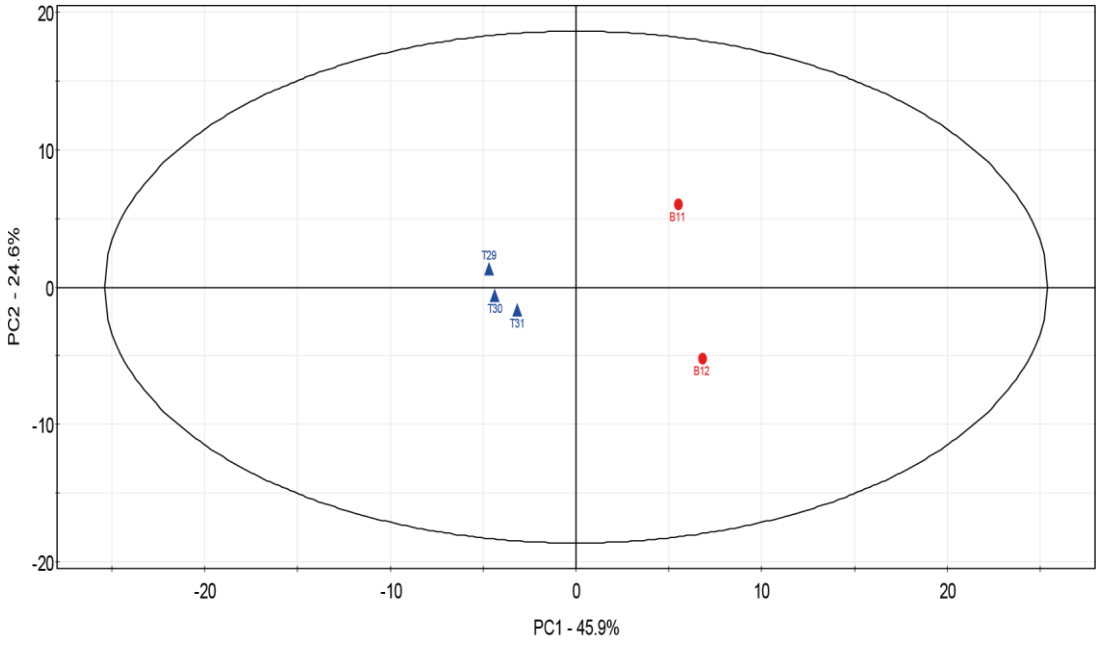


Figure 6-21. PCA scores plot and HCA dendrogram for batch 11E20. Clear separation of two bottled water brands, Fiji and evian®, is shown, as well as the clustering of all tap water samples tested. Tap water samples T4 and T6 are seen on the HCA dendrogram to be most closely related; this conclusion can be confirmed by the sample information gathered, where both of these samples were collected from Brisbane CBD.

2011 Batch #2 – 513FRI



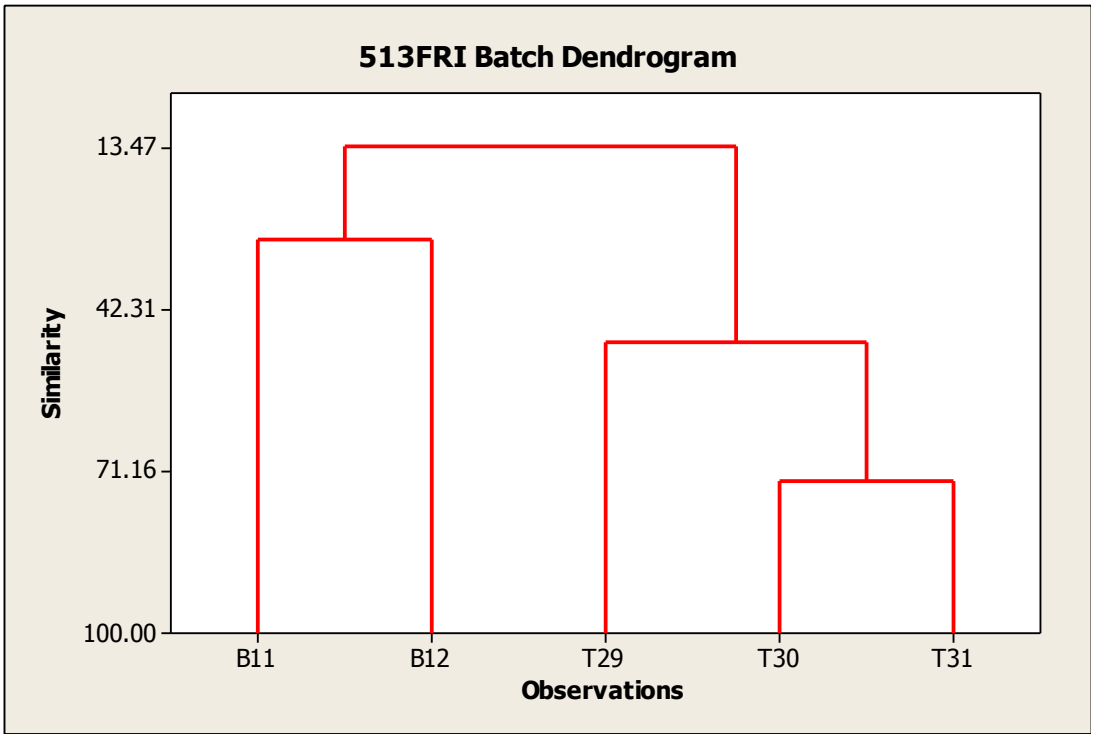
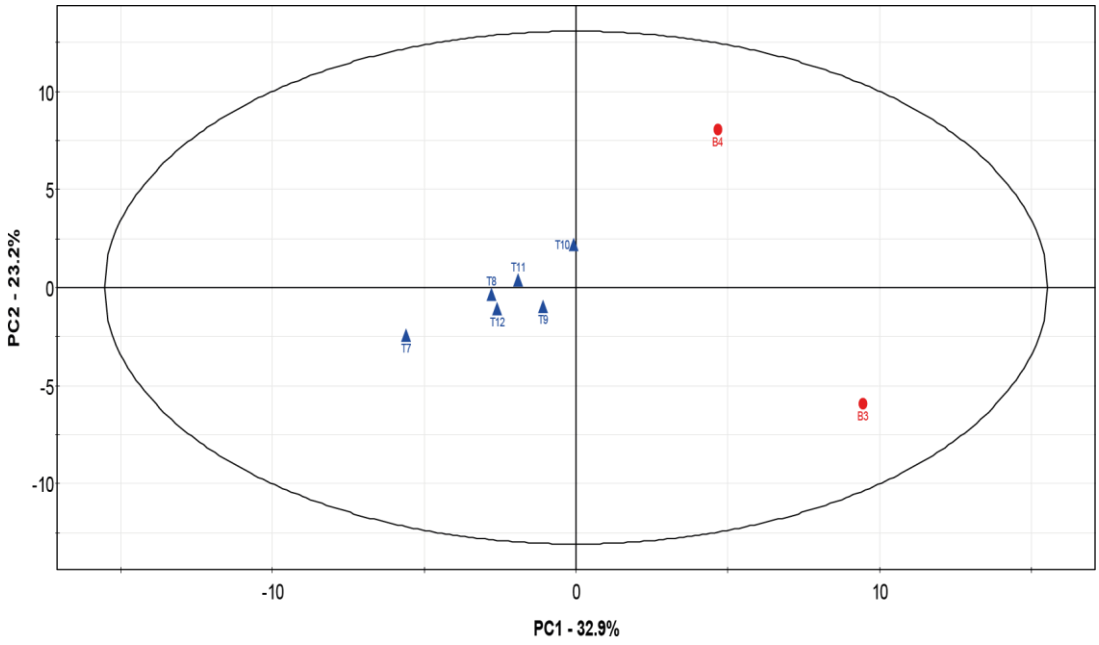


Figure 6-22. Both the PCA scores plot and the HCA dendrogram demonstrate the separation of two bottled water brands, Fiji and evian®, from tap water samples collected for batch 513FRI.

2011 Batch #3 – 513TUE17



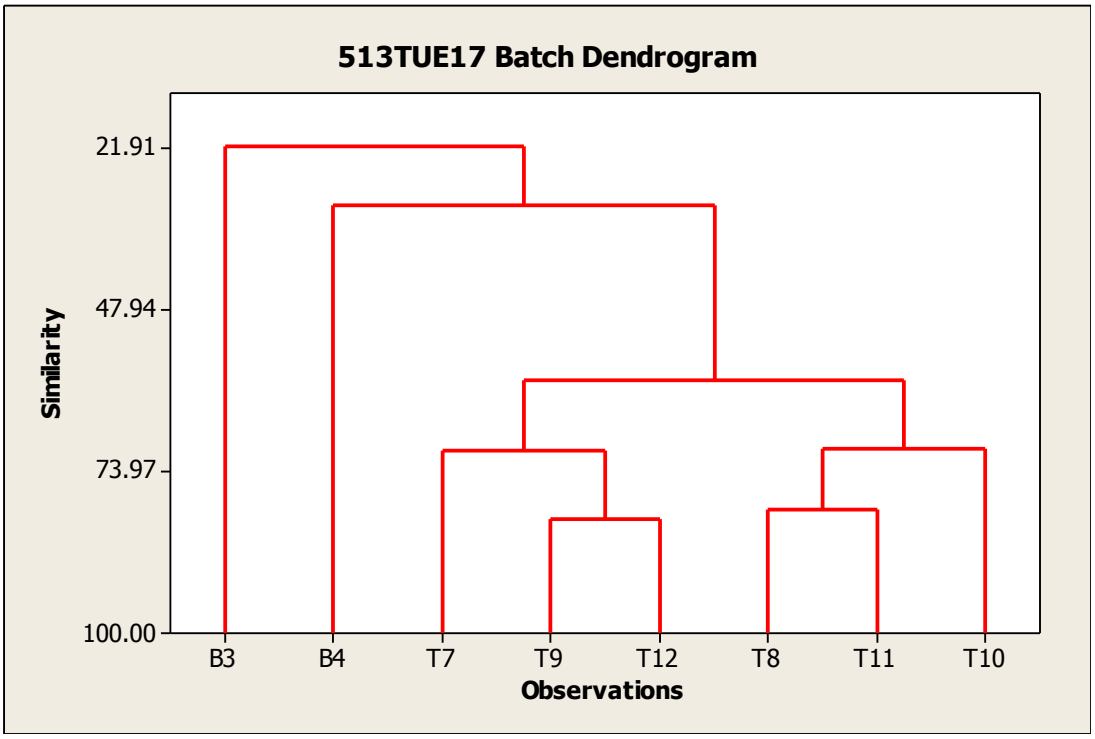
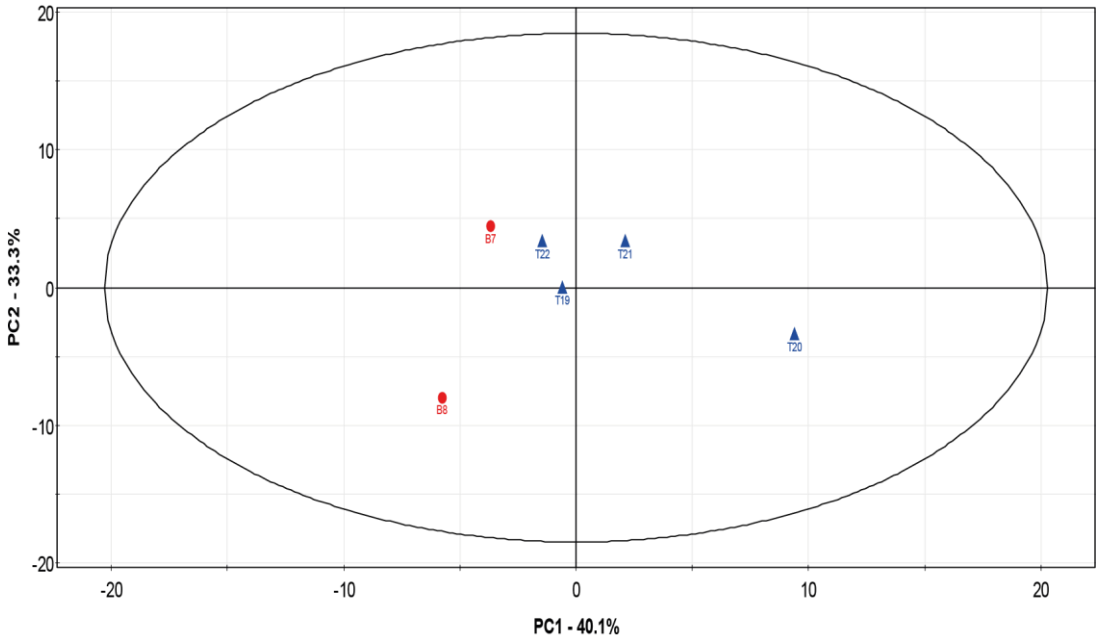


Figure 6-23. The PCA scores plot and HCA dendrogram for batch 513TUE17 show the distinction between two bottled water brands, Fiji and evian®, and the tap water samples analysed.

2011 Batch #4 – 51330511



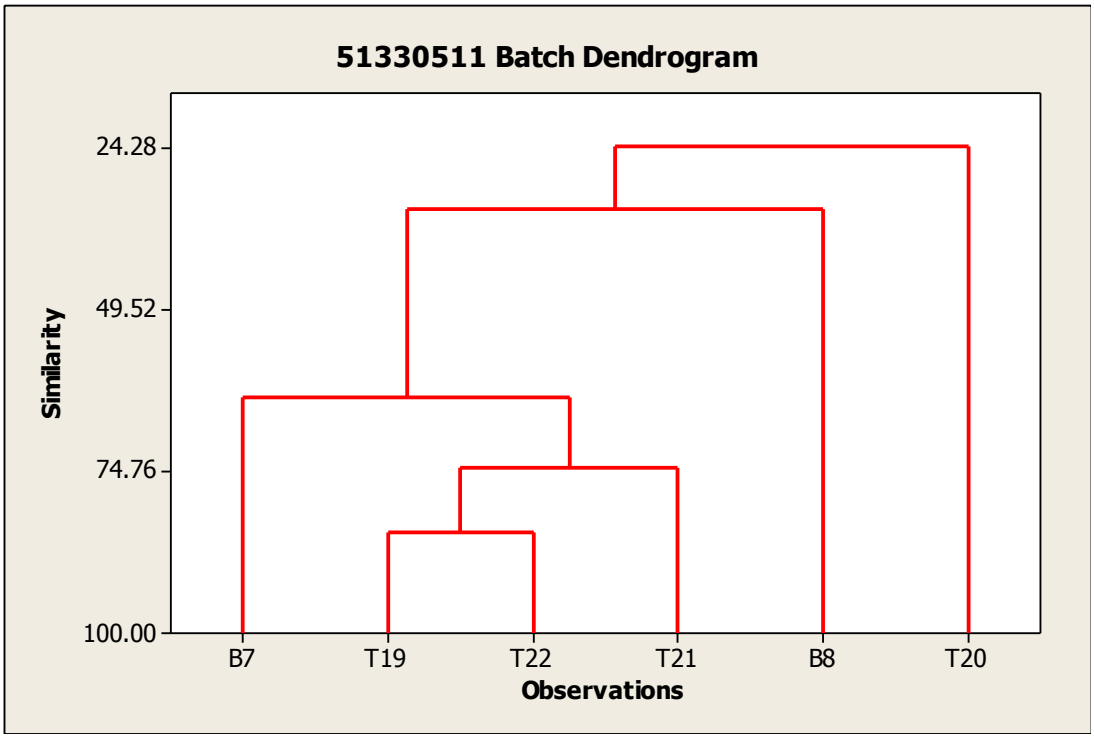
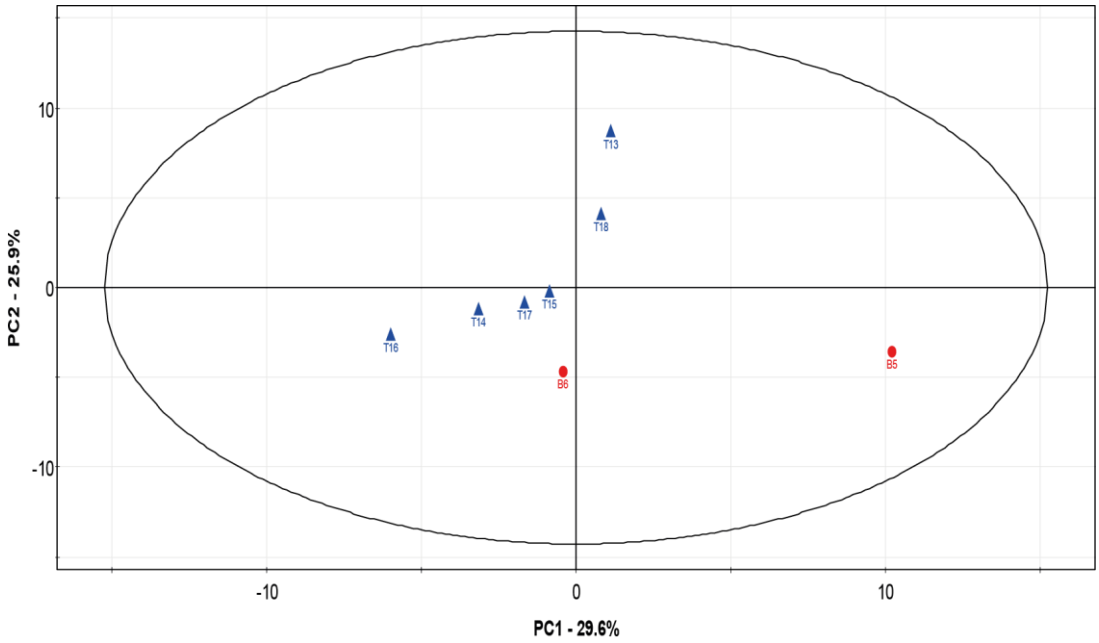


Figure 6-24. In batch 51330511, the PCA scores plot and HCA dendrogram show the commonly observed separation of bottled water and tap water samples. Unusually, tap water sample T20 is distinct from the tap water cluster. Sample information explains that sample T20 was collected from Prince Charles hospital, Chermside, and may therefore be of a different quality to household tap water.

2011 Batch #5 – F060511



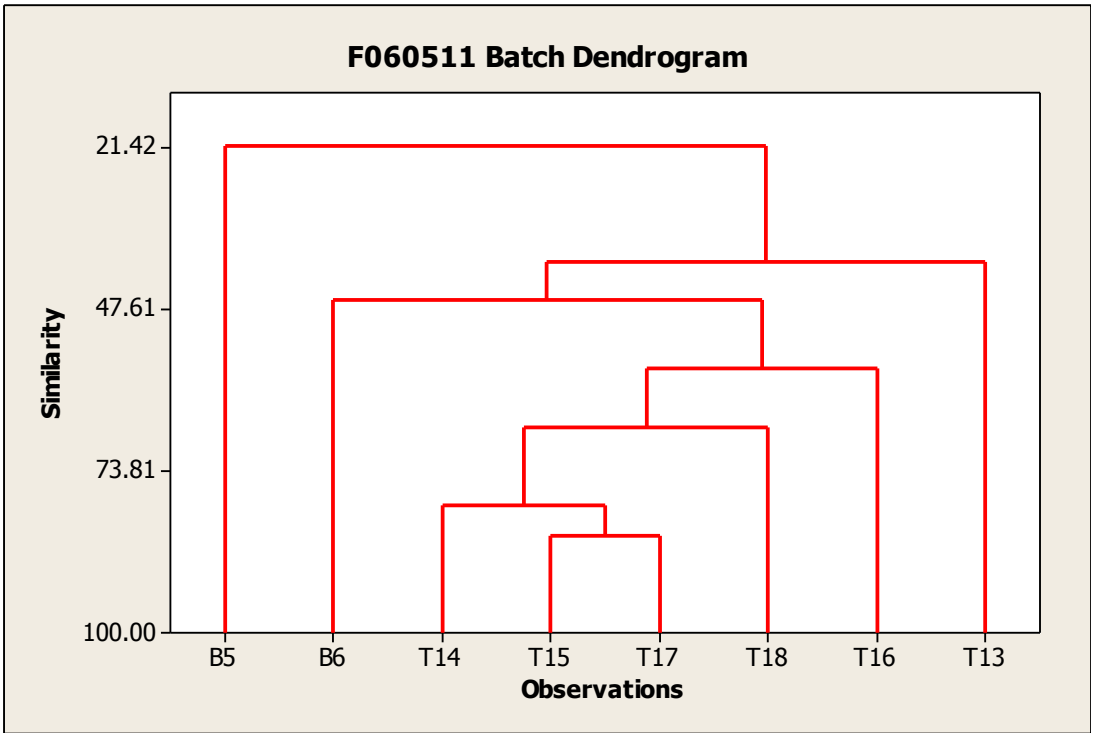
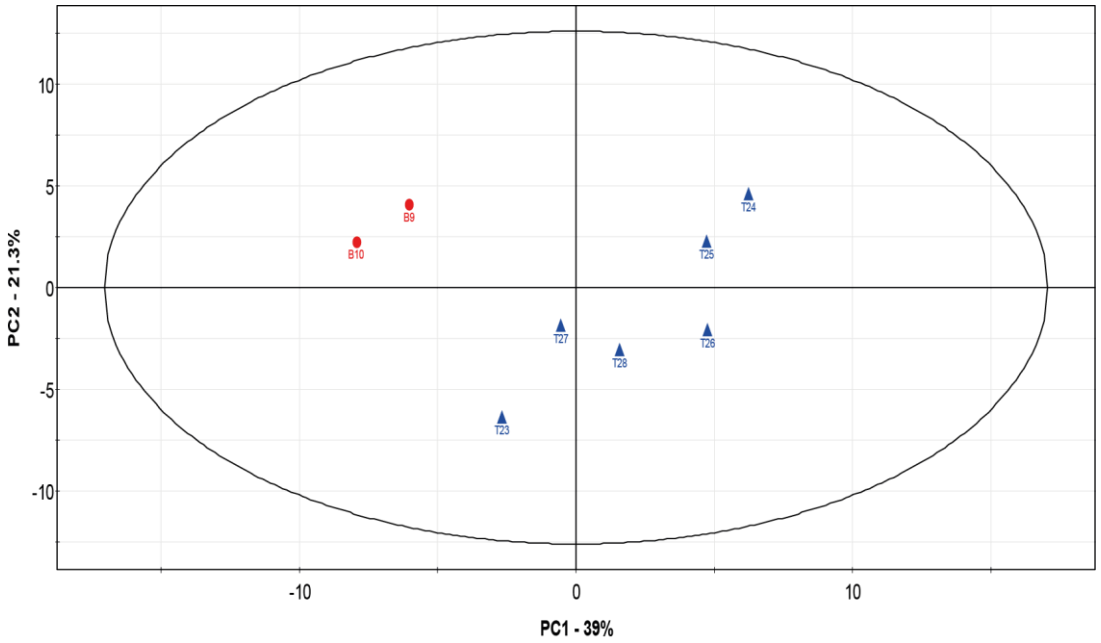


Figure 6-25. The tap water samples analysed for batch F060511 do not form a distinct cluster, as evidenced by the PCA scores plot and HCA dendrogram. One bottled water sample, evian®, is shown to be similar to the tap water samples tested. Overall, the samples investigated have not formed clusters, and this is especially apparent on the dendrogram, where all samples have comparable, almost even, levels of similarity with one another.

2011 Batch #6 – PQB513



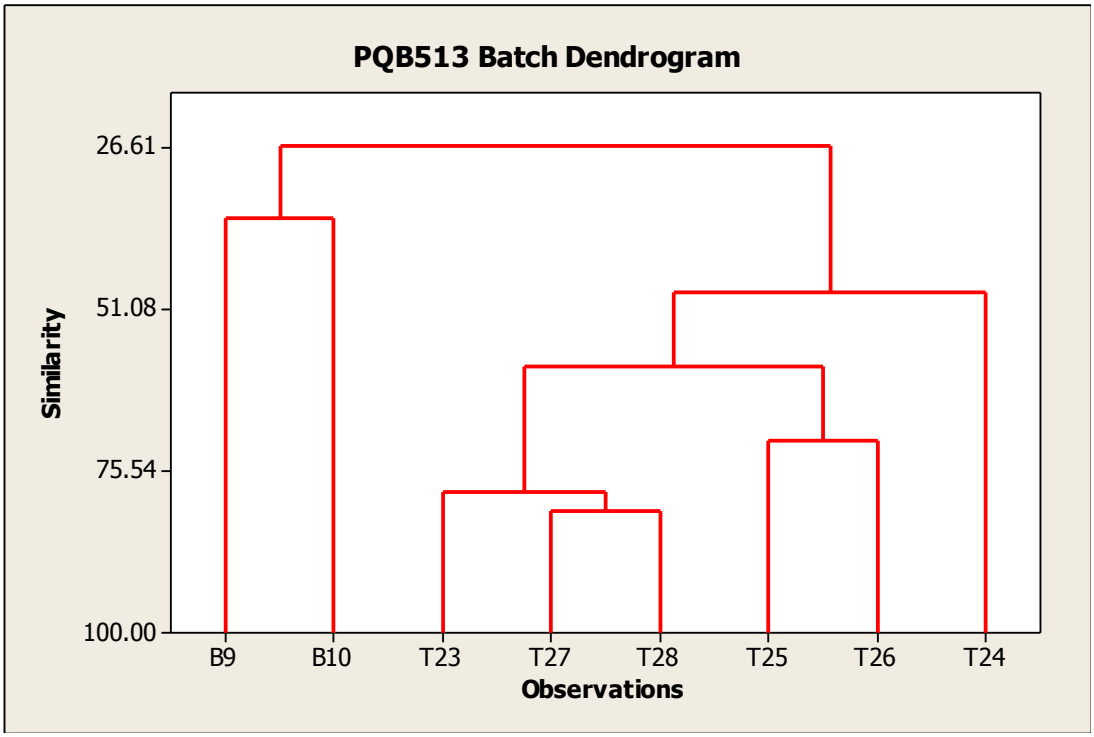
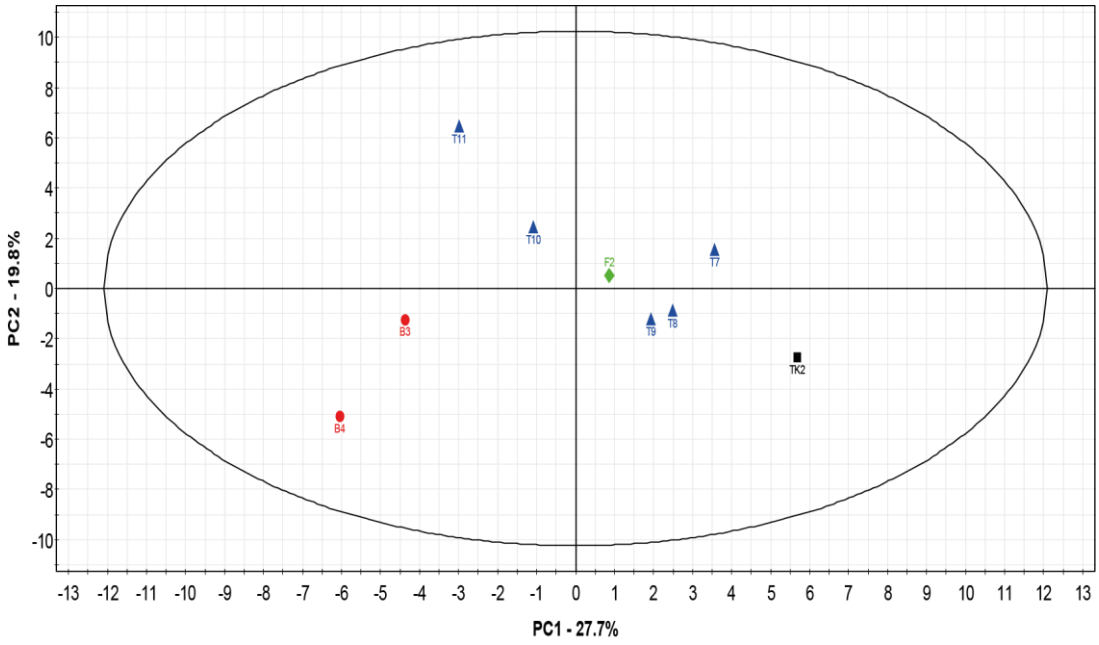


Figure 6-26. PCA scores plot and HCA dendrogram showing the separate clustering of tap and bottled water samples for batch PQB513.

2012 Batch #1 – 27Apr12



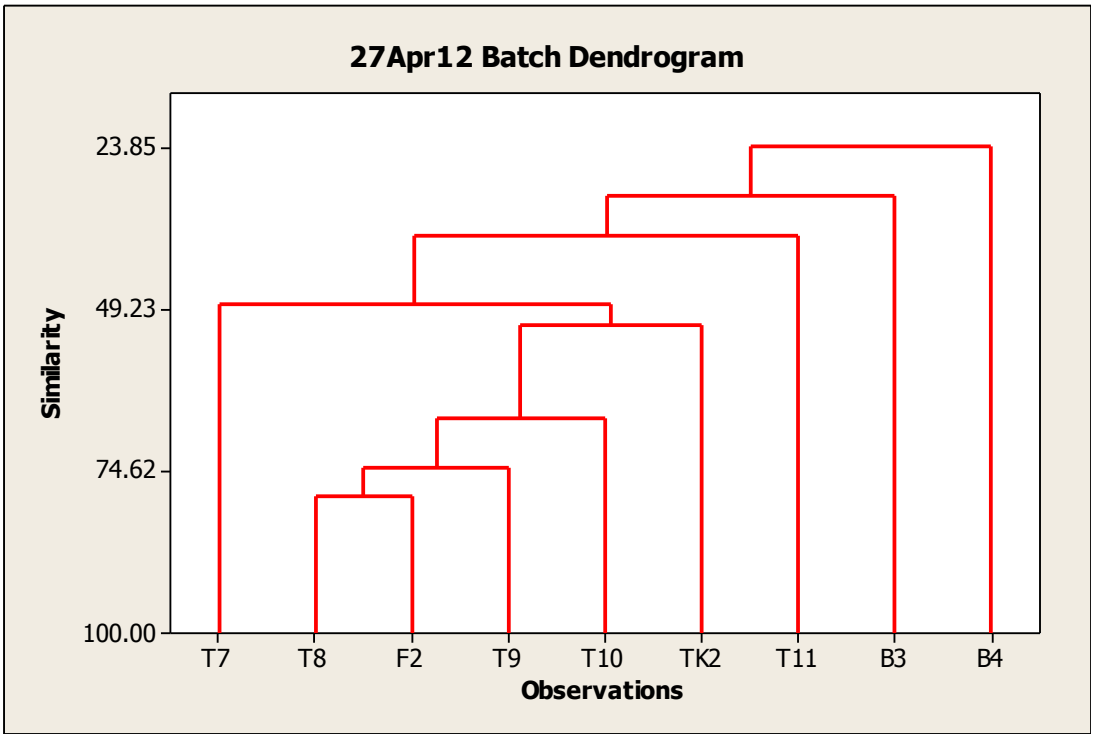
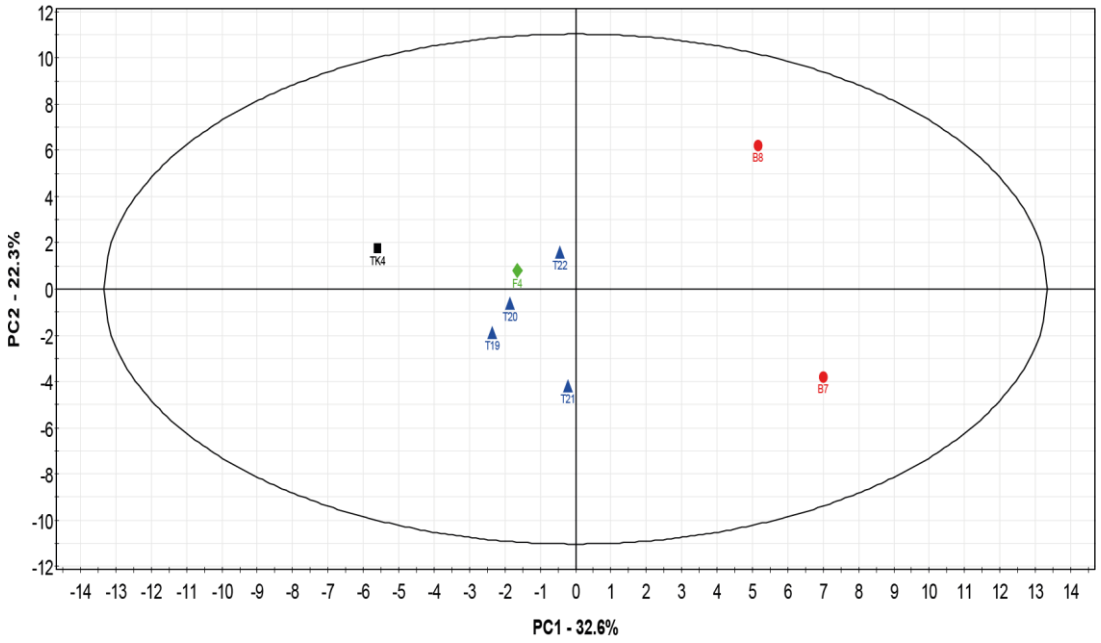


Figure 6-27. The tap, tank, filtered and bottled water samples collected for batch 27Apr12 are loosely clustered on the PCA scores plot and HCA dendrogram. The bottled water samples are obviously separate, yet the tap, tank and filtered samples, collected from different suburbs, are intermixed.

2012 Batch #2 – 150512



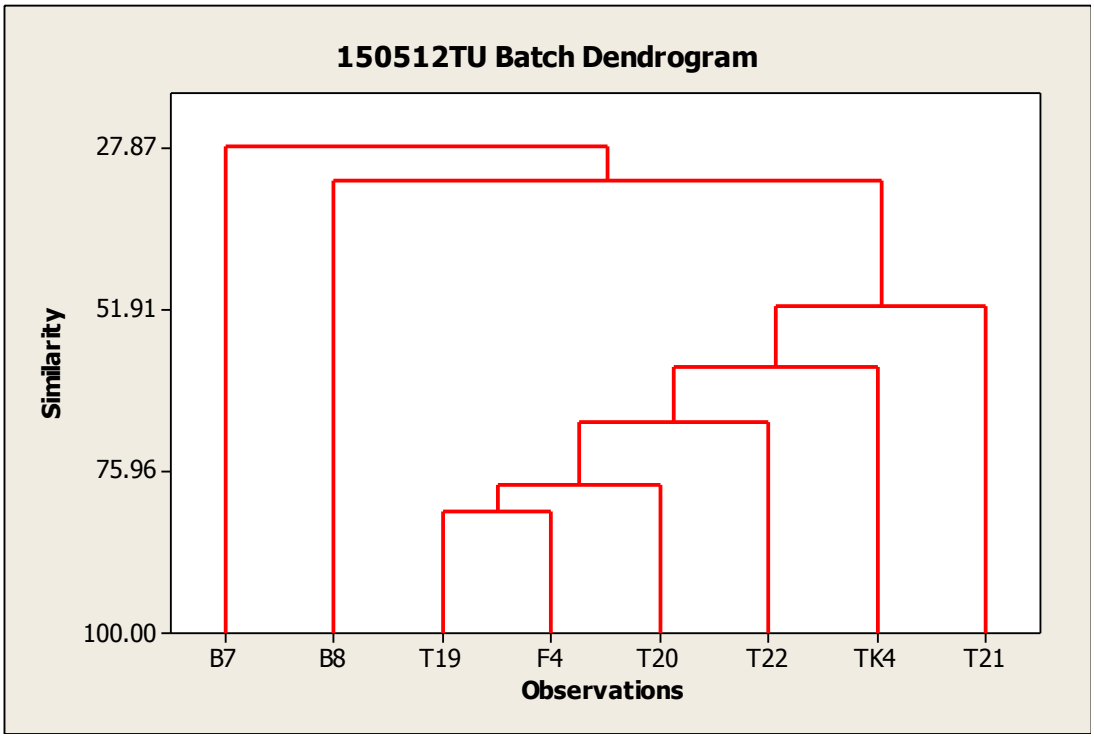
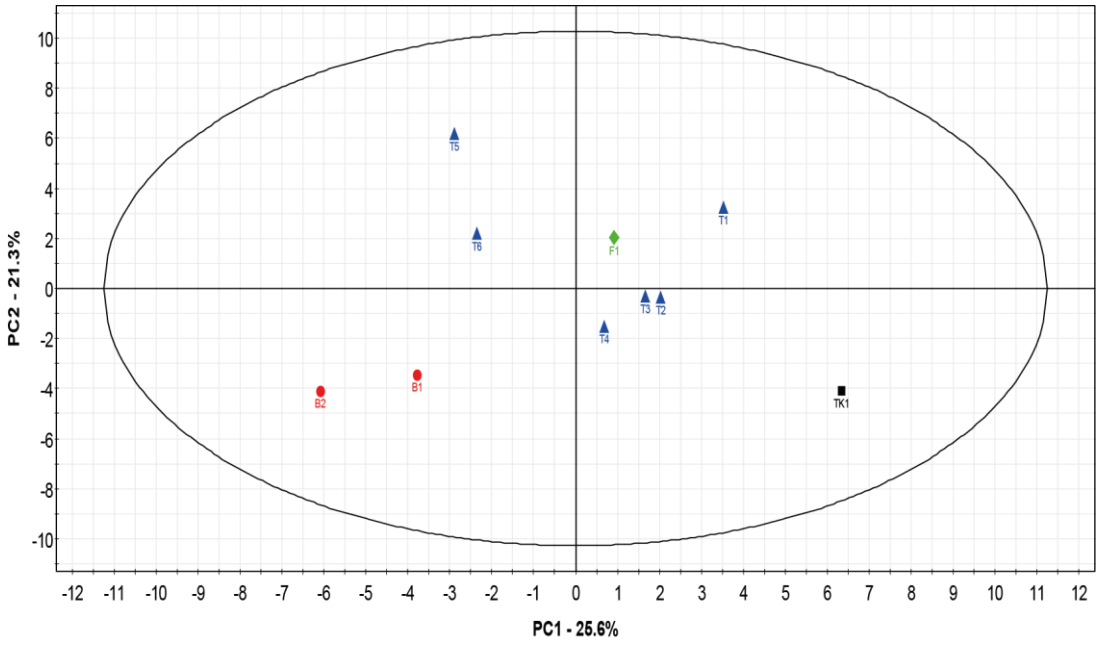


Figure 6-28. PCA scores plot and HCA dendrogram showing the clear clustering of the bottled water samples analysed, while the tap, tank and filtered water samples of batch 150512 are loosely clustered.

2012 Batch #3 – 170412



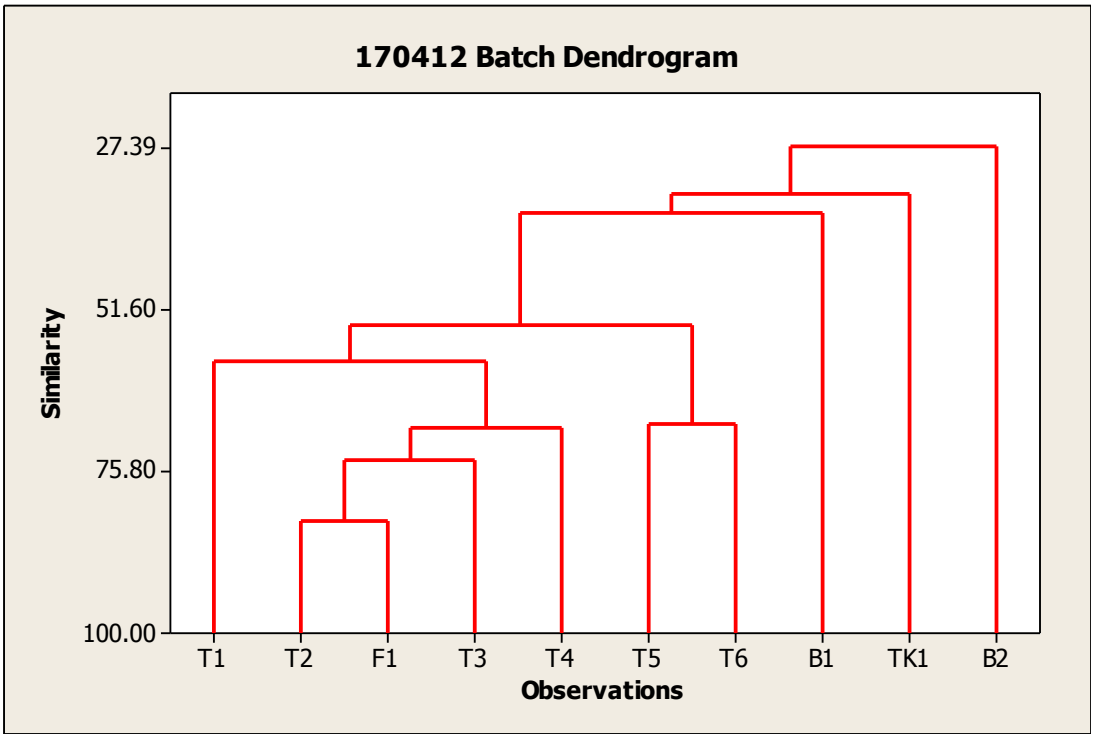
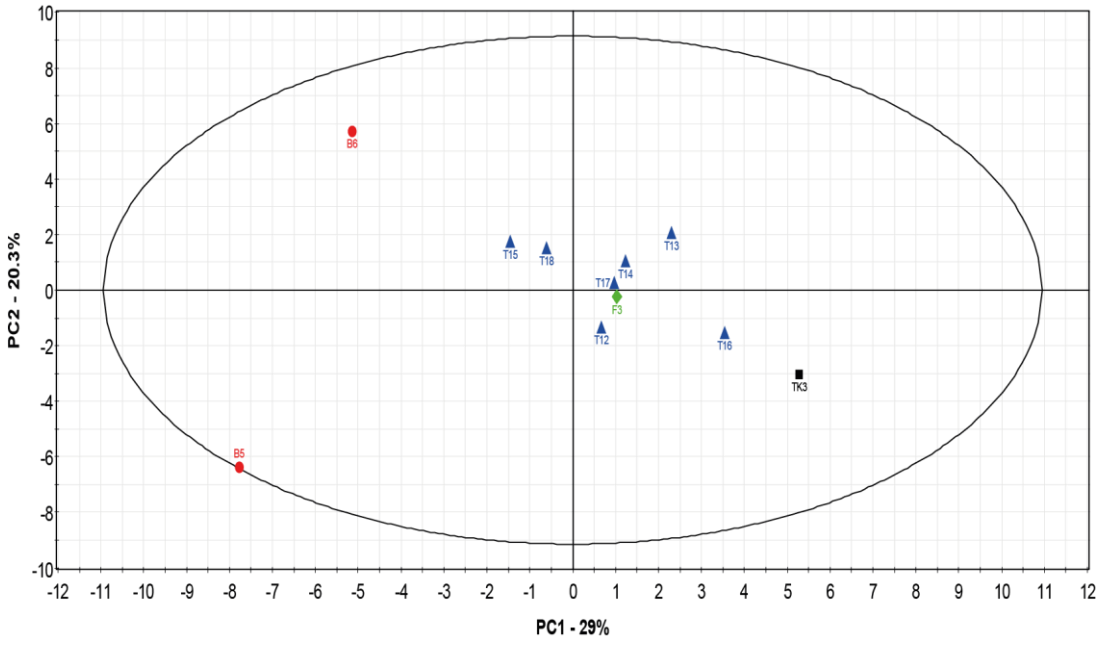


Figure 6-29. PCA scores plot and HCA dendrogram for batch 170412 show that the bottled and tank water samples are distinct from the tap and filtered water samples. Loose clustering is observed between the filtered water and tap water samples.

2012 Batch #4 – 01052012



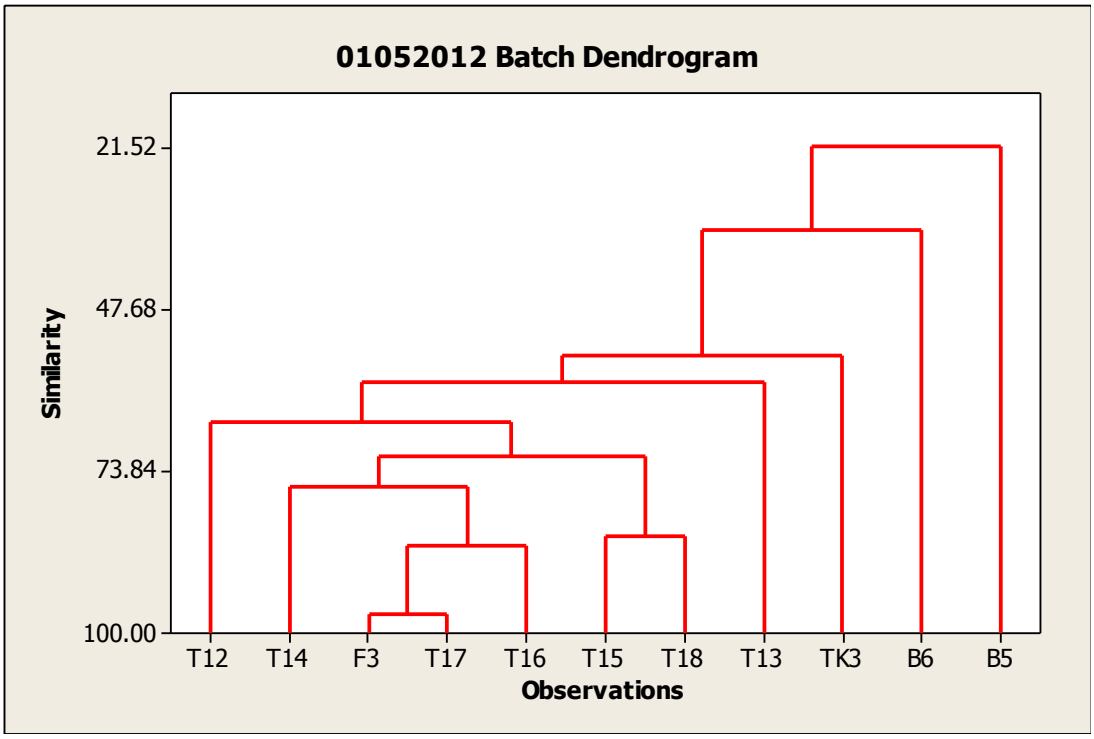


Figure 6-30. The two brands of bottled water are separate from the remaining samples, as is the tank water sample tested for batch 01052012. The PCA scores plot and HCA dendrogram also show the general clustering of the tap and filtered water samples collected.

C-2 Sample Collection Information – Tables and Area Maps

In 2013, sample collection was undertaken on a June long weekend, beginning on Friday June 7 with raw and treated water sample collection, through to Monday June 10 with potable sample collection. Mains water sample collection took place on Tuesday June 11, and bottled water was purchased on Thursday 13 June. Complete sample information is contained Table 6-2 to Table 6-3.

Table 6-2. The postcodes of residences from which potable water samples were collected and the corresponding sample codes are presented. Samples coloured blue and white were collected on Saturday June 8, 2013; samples coloured purple and white were collected on Sunday June 9, 2013; samples coloured green and white were collected on Monday June 10, 2013; and finally, samples coloured pink and white were collected by employees of H_2Flow throughout the week leading up to and including personal sample collection (from June 5 to June 11).

E.g.	4055	T1	F1	TK1
Resident visited	**Postcode**	**Tap**	**Filtered**	**Tank**
1	4280	T1		TK1
2	4270		F1	TK2 & TK3
3	4128	T2	F2	
4	4110	T3		
5	4078	T4		
6	4074	T5		
7	4074	T6	F3 & F4	
8	4069	T7		
9	4070	T8	F5	TK4
10	4075	T9		
11	4068	T10	F6	
12	4068	T11		
13	4068	T12		
14	4122	T13		
15	4165	T14	F7	TK5
16	4160	T15		
17	4160	T16		
18	4178	T17	F8	TK6
19	4178	T18	F9	
20	4170	T19		
21	4171	T20		
22	4169	T21		
23	4169	T22		
24	4120	T23		
25	4103	T24		

Resident visited	Postcode	Tap	Filtered	Tank
26	4105	T25	F10	TK7
27	4069	T26	F11	
28	4069	T27	F12	TK8
29	4069	T28	F13 & F14	
30	4068	T29	F15	
31	4066	T30	F16	
32	4064	T31		
33	4059	T32		
34	4059	T33	F17	TK9
35	4064	T34	F18	
36	4520		F19	TK10 & TK11
37	4060	T35	F20	
38	4010	T36		
39	4030	T37		
40	4030	T38	F21	
41	4051	T39		
42	4059	T40	F22	
43	4059	T41		TK12
44	4059	T42		
45	4059	T43		
46	4059	T44	F23	
47	4503	T45		
48	4017	T46	F24	
49	4018	T47		
50	4018	T48		
51	4034	T49	F25	
52	4034	T50	F26	TK13
53	4035	T51		
54	4055	T52	F27	TK14
55	4055	T53	F28	

Resident visited	Postcode	Tap	Filtered	Tank
56	4520	T54	F29	TK15
57	4520	T55		
58	4520		F30	TK16 & TK17
59	4520		F31	TK18 & TK19
60	4520			TK20
61	4061	T56		
62	4061	T57	F32	TK21
63	4061	T58	F33	
64	4054	T59		
65	4055	T60		TK22
66	4055	T61		TK23
67	4055	T62	F34	TK24
68	4055	T63	F35	TK25
69	4055	T64		TK26
70	4055	T65		
71	4055	T66	F36	TK27
72	4055	T67		TK28
73	4055	T68		
74	4055	T69		
75	4055	T70		
76	4055	T71		
77	4054	T72		TK29
78	4053	T73		
79	4053	T74	F37	
80	4053	T75	F38 & F39	
81	4053	T76		TK30
82	4053	T77		
83	4053	T78	F40 & F41	TK31
84	4053	T79	F42	
85	4051	T80		TK32

Resident visited	Postcode	Tap	Filtered	Tank
86	4053	T81	F43	
87	4053	T82 & T83		
88	4053	T84		
89	4051	T85		
90	4000	T86	F44	
91	4074		F45	
92	4053	H1		
93	4300	H2		
94	4110	H3		
95	4217	H4		
96	4164	H5		
97	4030	H6		
98	4073	H7		
99	4073	H8		
100	4005	H9		
101	4174	H10		
102	4169	H11		
103	4155	H12		
104	4156	H13		
105	4073	H14		
106	4178	H15		
107	4007	H16		
108	4069	H17		
109	4306	H18		
110	4108	H19		

Table 6-3. This table corresponds to the sample information displayed in Table 6-2. Here, the order and postcodes of residences visited are the same as above, and the responses to the survey questions asked of the participants are displayed. Colour coding in accordance to dates samples were collected is also the same as in Table 6-2.

E.g.	4055	80s	Cu? Pb? PVC?	Monthly, yearly, etc.	Laundry, toilet?	Taste, Colour, Odour?
Resident visited	**Postcode**	**Decade house was built?**	**Knowledge of pipes?**	**Frequency of filter change?**	**Uses of tank water?**	**Comments**
1	4280	2010 -	PVC	N/A	Kitchen Tap	Tap water in Mother-In-Laws "annex"; tank water connected to main kitchen tap.
2	4270		PVC	don't know	TK2: concrete tank; TK3: plastic tank	TK2: water off roof, rain water; TK3: water bought, stored here (Val's house)
3	4128		Cu	Brita filter	N/A	Brita jug filter was 75% through its life span. Tap water has gotten better, but usually drink filtered water.
4	4110	60s	Cu	N/A	N/A	Can see tips of copper pipes on outside of taps.
5	4078	00s	(probably) PVC	N/A	N/A	First people in their unit.
6	4074		PVC	N/A	N/A	
7	4074		PVC	F3: tap - never; F4: Brita	N/A	Mostly drink water from Brita jug (F4), not tap filter.
8	4069	70s	Cu	N/A	N/A	
9	4070	2007	PVC	supposed to change after 12 months, has been 18 months	Laundry, toilets, external hoses	
10	4075					Outside tap.
11	4068				N/A	F6: Brita jug; relatively new apartment building, most likely PVC pipes

Resident visited	Postcode	Decade house was built?	Knowledge of pipes?	Frequency of filter change?	Uses of tank water?	Comments
12	4068					Much older apartment buildings, most likely copper pipes.
13	4068					Much older apartment buildings, most likely copper pipes.
14	4122					
15	4165		PVC	every 8 weeks (fairly diligent)	Gardens, dog	Chlorine smell in tap after long disuse.
16	4160	70s-90s				Original house was built in the 70s, built in underneath in the 90s - sample was from downstairs of house.
17	4160	90s				
18	4178		PVC	new fridge filter, charcoal filter	Filling pool, garden	Old pipes rusted, replaced with PVC about 8 years ago.
19	4178		PVC	attached to tap		Filter was due to be changed in May (sample collected 9/6).
20	4170		Cu			Tastes delicious.
21	4171		Cu			
22	4169					
23	4169		(probably) Cu			Outside tap.
24	4120		Cu			

Resident visited	Postcode	Decade house was built?	Knowledge of pipes?	Frequency of filter change?	Uses of tank water?	Comments
25	4103	00s				
26	4105		Cu	6 months; was changed 3-4 months ago	Toilets	Sediment and Carbon filter used.
27	4069		PVC	6 months		
28	4069		PVC	don't know	Garden	Drink filtered water.
29	4069		PVC	F13: tap, F14: fridge		F14: only 6 month old fridge, always drink this water, not tap or filter tap.
30	4068	70s	Cu	6 months, due for change		Drink filtered water.
31	4066		PVC	1 month old		Brita Carbon filter, always drink this water.
32	4064					
33	4059		Cu			
34	4059		PVC	6 months	Laundry, garden	
35	4064		(probably) PVC			
36	4520		Cu	don't know	TK10: whole house; TK11: fire emergency	TK10: hooked up to house taps (concrete tank); TK11: galvanised iron, fire and pool.
37	4060	80s	PVC	not often	N/A	

Resident visited	Postcode	Decade house was built?	Knowledge of pipes?	Frequency of filter change?	Uses of tank water?	Comments
38	4010		Cu			Rental.
39	4030		(probably) Cu			
40	4030	00s	PVC	yearly		
41	4051		Cu	N/A	N/A	
42	4059		Cu	not in three years		Drink tap water.
43	4059					
44	4059	90s (?)				
45	4059	90s (?)				
46	4059			don't know		Filtered water came from Brita jug.
47	4503					
48	4017		Cu	1 year ago		
49	4018	90s-00s				
50	4018					
51	4034	90s				

Resident visited	Postcode	Decade house was built?	Knowledge of pipes?	Frequency of filter change?	Uses of tank water?	Comments
52	4034	60s	Cu	never	outside toilet, garden	Have never changed filter on tap at sink.
53	4035	80s				
54	4055	00s		new filter (only weeks old)	Laundry, pool	
55	4055	90s (92)	Cu, outside: black plastic	6 months		Drink filtered water. House located at the end of a cul-de-sac up hill - effects water quality.
56	4520		Cu		Garden, not really used	Water filter in fridge. Know that their water comes from North Pine Dam, believe is a good WTP, water never tastes "chloriney", etc.
57	4520	00s	PVC			House can be run on town water or tank water. Can switch between and can take a few hours for supply to change over.
58	4520	90s		every 12 months (last changed Oct 12)	TK16: used in whole house.	TK17: "spare" tank, hasn't been used in years.
59	4520			every 6 months	TK18: used in whole house.	TK19: "spare" tank, hasn't been used in years.
60	4520					TK20: water filtered twice and connected to whole house.
61	4061					Outside tap.
62	4061		PVC/Cu	Once a year.	Washing machine, garden, washing cars/bikes.	PVC from street to house, copper inside the house.
63	4061		Cu	Yearly. Last changed in Jan 12.		Know that their water is from the Enoggera Dam supply.
64	4054		Cu			

Resident visited	Postcode	Decade house was built?	Knowledge of pipes?	Frequency of filter change?	Uses of tank water?	Comments
65	4055	80s	Cu		Laundry, gardens, wash cars.	**Duplicate **T60a** also collected from this home.**
66	4055	80s (?)				
67	4055	80s	Cu	6 months	Garden.	
68	4055	80s	Cu	12 months	Garden.	
69	4055	80s	Cu		Garden.	
70	4055	00s	PVC			
71	4055	00s	PVC		Garden and pool.	
72	4055	00s	PVC		Garden and pool.	
73	4055		Cu			
74	4055		PVC, Cu and stainless steel connector.			
75	4055					Outside tap.
76	4055	60s	Cu			After periods of long disuse: brown colour, takes time to flush out using all taps in the house.
77	4054		Cu		Garden.	

Resident visited	Postcode	Decade house was built?	Knowledge of pipes?	Frequency of filter change?	Uses of tank water?	Comments
78	4053					
79	4053		Cu	12 months		
80	4053		PVC	F38: 2 years & F39: 4 months		F38: slow – need new filter.
81	4053		Cu		Garden/outside	
82	4053					Outside tap.
83	4053		PVC	(both) every 6 months	Toilets.	F40: on the sink; F41: on the fridge.
84	4053		Cu	every 6 months		
85	4051		Cu		Under house (on front), garden.	
86	4053		Cu	12 months		
87	4053		T82: Cu; T83: PVC			T82: copper pipes in main house; T83: PVC pipes in granny flat.
88	4053					Outside tap.
89	4051		PVC			New apartment block.
90	4000		PVC	unknown		New office block, about 12 months old - on sink filter.
91	4074			unknown		[Didn't collect myself]

Resident visited	Postcode	Decade house was built?	Knowledge of pipes?	Frequency of filter change?	Uses of tank water?	Comments
92	4053					Mains Water
93	4300					
94	4110					
95	4217					
96	4164					House Tap
97	4030					
98	4073					Truck sample from tank
99	4073					Water sample (from mains, before in truck)
100	4005					
101	4174					
102	4169					
103	4155					
104	4156					
105	4073					

Resident visited	Postcode	Decade house was built?	Knowledge of pipes?	Frequency of filter change?	Uses of tank water?	Comments
106	4178					
107	4007					
108	4069					
109	4306					
110	4108					

As demonstrated in Table 6-2 and Table 6-3, potable tap, tank and filtered water samples were collected from 110 locations in the greater Brisbane area, extending from Kallangur in the north, the Gold Coast in the south, Victoria Point in the east, and Mt Crosby out west. Figure 4-16 and Figure 4-17 presented in Chapter Four are maps displaying the residences visited in order to better visualise the number and spread of the samples collected.

In addition to collecting potable water samples from homes in the greater Brisbane area, raw water samples were collected as well as treated water samples. All raw water sample collection information, including a description of the dam, lake, river or creek, and the surrounding area, is presented in Table 6-4; Figure 4-18 in Chapter Four is a map displaying the raw water collection sites.

Additionally, mains water samples were collected with the assistance of water transportation company H_2Flow. Figure 4-20 in Chapter Four, and Table 6-5 depict the sample collection sites and corresponding information, respectively.

Table 6-4. The sites, time of collection, location and description of the surrounds for each raw water sample collected, as well as for the two treated water samples collected from Mt Crosby West Bank WTP.

	Site	Address	Time Collected on 7/6/13	Label	Description of area/location and accompanying comments:
1	Mt Crosby Westbank WTP	Allawah Rd, Chuwar, Ipswich	9:25am	MCR	Raw water collected from Mt Crosby Westbank WTP.
2	Mt Crosby Westbank WTP	Allawah Rd, Chuwar, Ipswich	9:48am	CH1	Treated water collected from Cameron's Hill Reservoir 1.
3	Mt Crosby Westbank WTP	Allawah Rd, Chuwar, Ipswich	9:50am	CH2	Treated water collected from Cameron's Hill Reservoir 2.
4	Brisbane River @ Colleges Crossing	Colleges Crossing, Chuwar	10:10am	CC	Low bridge, flowing water, pipe moving in the middle of the water, overall brown appearance although the water appears clear.
5	Oxley Creek	Oxley Creek Common, Sherwood Rd, Rocklea	11:05am	OC	Between sewerage works and Brisbane River - high tide at 9:32am on 7/6/13, so creek was flowing out to Brisbane River when sample was collected. Tidal, mangroves, brown turbid water.
6	Wivenhoe Dam	Wivenhoe Dam Information Centre, Brisbane Valley Highway	1:30pm	WD	Picnic area, public access, wildlife (birds) present. Water has brown appearance although is relatively clear.
7	Lake Somerset "The Spit"	Esk-Kilcoy Rd	2:35pm	LS	Public access, picnic, wildlife, recreational areas and boat ramp; also ongoing construction to incoming roads. Water overall brown in appearance due to dirt bottom lake, but is very nice clear water.

	Site	Address	Time Collected on 7/6/13	Label	Description of area/location and accompanying comments:
8	Baroon Pocket Lake and Dam	Baroon Pocket Rd, Monteville	4:15pm	BP	Public access, picnic, wildlife, recreational areas, boat ramp. Dam wall visible from lake shore. Sand (not dirt bottom) lake. Overall brown appearance (natural) and water is relatively clear.
9	Ewan Maddock Dam	Maddock Park, Mooloolah Connection Rd (off Steve Irwin Way), Beerwah	5:10pm	EM	Public access, no animals (horses, dogs) allowed. Wildlife present. WTP is right alongside dam wall. Sand lake (rather than dirt bottom). Surrounded by forest, water relatively clear.
10	Ewan Maddock Dam	Maddock Park, Mooloolah Connection Rd (off Steve Irwin Way), Beerwah	5:25pm	EM2	Duplicate of above sample for Quality Control (QC) purposes.
11	Lake Samsonvale - Forgan Cove	Forgan Cove, Forgan Rd, Joyner	11:50am	LS FC	Wildlife, plant life in and around water, dirt bottom lake – collected 10/6/13. (North Pine Dam).
12	Lake Samsonvale - Bullocky Rest	Bullocky Rest, Forgan Rd, Joyner	12:05pm	LS BR	Wildlife, plant life in and around water, dirt bottom lake. Recreational area, playground and BBQs, fishing allowed – collected 10/6/13. (North Pine Dam).

Mains water samples were collected from various suburbs that had not been visited during potable water sample collection, ensuring the widest possible spread of samples.

Table 6-5. The post code, time of collection and descriptive comments for each water main visited and sampled with H_2Flow on Tuesday June 11, 2013.

	Postcode	Time	Label	Description of area/location and accompanying comments:
1	4074	10:30am	MWSP	Fairly clean, used regularly.
2	4076	10:50am	MWW	Outside RPG facility.
3	4077	11am	MWI	Old area, homes built in the 50s.
4	4077	11:15am	MWD	Brand new estate = new lines.
5	4077	11:25am	MWR1	Older area, 70s.
6	4077	11:30am	MWR2	New area, new estate <10 years old.
7	4075	11:40am	MWOx	40s-50s, old area.
8	4075	12pm	MWC	Old area, off Corinda Station. Leaking hydrant after sample was taken.
9	4075	12:10pm	MWS	Hydrant has been replaced, is very new.
10	4075	12:20pm	MWG	Ants nest in hydrant, some dirt (black specks) visible in sample.
11	4068	12:30pm	MWCh	Looks as if it has been (recently) cleaned out.
12	4066	12:40pm	MWA1	Hydrant at crossroads, is fairly clean.
13	4066	12:50pm	MWA2	Brand new hydrant, after flushing, water still appears dirty, sample taken anyway.
14	4066	12:50pm	MWA3	Same hydrant as above, second sample collected when water was visibly clearer/cleaner.
15	4064	12:55pm	MWM	Older area, some new houses, hydrant fairly clean.
16	4401	1pm	MWRos	Hydrant had water in it, looked like how we left them, perhaps someone was there shortly before us? Took longer to become clean, clumps of dirt.
17	4065	1:10pm	MWB	Dirty, had to clean it out first, but then all good and clear.

Finally, a variety of bottled water brands were purchased from Coles in Brisbane city and tested for a complete analysis of potable water sources available in South East Queensland.

Table 6-6. Bottled water brands purchased for this research on Thursday June 13, 2013. All samples were still water except for two that were lightly carbonated.

	Brand	Label	Accompanying description/comments:
1	Aroona Sports Body Quencher	B1	
2	Frantelle Natural Spring Water	B2	
3	Coles Australian Natural Spring Water	B3	
4	Nobles Pureau Pure Water	B4	
5	evian® Natural Mineral Water	B5	
6	San Pellegrino	B6	Lightly carbonated
7	Pump Pure Water	B7	
8	Cocobella Coconut Water	B8	
9	Mount Franklin: Australia's Premium Spring Water	B9	
10	Santa Vittoria: Sparkling Italian Mineral Water	B10	Lightly carbonated
11	Cool Ridge Australian Spring Water	B11	

C-3 Comparisons to Independent Water Quality Reports, ANZECC/ARMCANZ (2000) Water Quality Guidelines for Toxicants and Sediment Concentrations

The following independent water quality reports are from Seqwater (Figure 6-31) and Queensland Urban Utilities (Figure 6-32), South East Queensland's main water supplier and distributor, respectively. A table detailing the pH and hardness of each raw water source, as well as the heavy metals in each sample that exceed the 95% protection level trigger values of the ANZECC/ARMCANZ (2000) water quality guidelines for toxicants is then presented (Table 6-7). Additionally, a map (Figure 6-33) from the DNRM report entitled: Queensland Mineral Prospectivity Atlas shows sediment sampling sites comparable to raw water collection sites in this research.

WATER REPORTING ZONE 2 - June 2013

	Monthly performance					Long-term performance (12 month)							
Parameter	Unit of measure	Number of samples	Minimum	Average	Maximum	Number of samples	Average	Annual result	Perfomance guideline used	Aesthetic guideline value	Number of aesthetic exceedence	Health guideline value	Number of health exceedence
Health Parameters (note that copper and manganese have both health and aesthetic guideline values)													
E.coli	orgs/100mL	36	<1	<1	<1	469	<1	100%	98	Not applicable		0 in 100ml	1
Fluoride	mg/L	48	0.5	0.8	0.9	603	0.7	1.00	95	Not applicable		1.5 mg/L	0
TTHMS	mg/L	12	0.04	0.10	0.13	149	0.07	0.13	95	Not applicable		0.25 mg/L	0
Lead	mg/L	12	<0.001	<0.001	<0.001	149	<0.001	0.00	95	Not applicable		0.01 mg/L	0
Copper	mg/L	12	<0.001	0.001	0.002	149	0.001	0.00	95	1 mg/L	0	2 mg/L	0
Manganese	mg/L	36	<0.001	0.002	0.004	469	0.005	0.01	95	0.1 mg/L	0	0.5 mg/L	0
Aesthetic Parameters													
Hardness	mg/L as CaCO3	11	44	169	264	148	94	Not applicable		200 mg/L	8		
pH		36	7.3	7.7	8.1	469	7.7	Not applicable		6.5 - 8.5	0		
Turbidity	NTU	36	<0.1	0.1	0.2	469	0.1	Not applicable		5 NTU	0		
Total Dissolved Solids	mg/L	27	122	324	576	368	237	Not applicable		600 mg/L	0		
True Colour	HU	36	<1	<1	2	469	<1	Not applicable		15 HU	0		
Alkalinity	mg/L as CaCO3	18	40	103	146	210	76	Not applicable		Not applicable			
Aluminium	mg/L	36	0.014	0.037	0.063	469	0.038	Not applicable		0.2 mg/L	0		
Iron	mg/L	36	<0.05	<0.05	<0.05	469	<0.05	Not applicable		0.3 mg/L	0		

Note: Reported values preceded by a < symbol indicate a result that is a non-detectable, as it is less than the limit of detection.
This report is a representation of the water reporting zone report for a month.
The measurement of 'orgs/100mL' summarises tests performed with the CFU and MPN measurements.

Figure 6-31. Monthly Seqwater Grid Report for Brisbane (Zone 2) for June 2013 (SEQ Water Grid Manager, 2013).

Queensland Urban Utilities
SEQ water grid Drinking Water Quality July 2012-June 2013

Aesthetic water quality

Aesthetic test description	Units	No of tests	Minimum	Maximum	Average	Aesthetic guideline	Health limit	Scheme compliant with ADWG 2011
Aluminium	mg/L	1045	0.005	0.86	0.04	0.2	ns	Yes
Chloride	mg/L	245	17	170	66	250	ns	Yes
Iron	mg/L	1045	0.0027	2.2	0.03	0.3	ns	Yes
pH	pH Unit	1956	6.6	8.8	7.74	6.5-8.5	ns	Yes
Total Dissolved Salts	mg/L	648	120	560	283	600	ns	Yes
Total Hardness	mg/L	545	44	250	124	200	ns	Yes
Turbidity	NTU	2036	<LOR	10	0.25	5	ns	Yes
Zinc	mg/L	546	<LOR	0.92	0.01	3	ns	Yes

Queensland Urban Utilities
SEQ water grid Drinking Water Quality July 2012-June 2013

Health-related water quality

Health related test description	Units	No of tests	Minimum	Maximum	Average	Aesthetic guideline	Health limit	Scheme compliant with ADWG 2011
Barium	mg/L	546	0.005	0.046	0.02	ns	2	Yes
Cadmium	mg/L	546	<LOR	<LOR	<LOR	ns	0.002	Yes
Chlorine (Total)	mg/L	10496	<LOR	4	1.1	ns	4.1	Yes
Chromium	mg/L	546	<LOR	0.005	<LOR	ns	0.05	Yes
Copper	mg/L	546	<LOR	1.1	0.02	1	2	Yes
Dichloroacetic Acid	ug/L	58	<LOR	33	11.4	ns	100	Yes
Escherichia coli	CFU/100mL	9104	n/a	n/a	n/a	ns	<1	Yes
Fluoride (as F)	mg/L	737	0.086	1.1	0.78	ns	1.5	Yes
Lead	mg/L	546	<LOR	0.12	0.001	ns	0.01	Yes
Manganese	mg/L	1045	<LOR	0.86	0.01	0.1	0.5	Yes
Monochloroacetic Acid	ug/L	58	<LOR	<LOR	<LOR	ns	150	Yes
Nickel	mg/L	546	<LOR	0.0072	<LOR	ns	0.02	Yes
Nitrate (as N)	mg/L	1430	<LOR	2	0.52	ns	50	Yes
Nitrite (as N)	mg/L	1430	<LOR	0.76	<LOR	ns	3	Yes
Sulfate (as SO4)	mg/L	95	21	96	36.44	250	500	Yes
Trichloroacetic Acid	ug/L	58	<LOR	20	<LOR	ns	100	Yes
Trihalomethanes (Total)	ug/L	201	15	170	78.6	ns	250	Yes

Queensland Urban Utilities
SEQ water grid Drinking Water Quality July 2012-June 2013

Other water quality

Test description	Units	No of tests	Minimum	Maximum	Average	Aesthetic guideline	Health limit	Scheme compliant with ADWG 2011
2-Methylisoborneol	ng/L	95	<LOR	24	4.2	ns	ns	n/a
Alkalinity	mg/L	238	34	140	77	ns	ns	n/a
Ammonia (Free, as N)	mg/L	1537	<LOR	0.9	0.18	ns	ns	n/a
Ammonia (Total, as N)	mg/L	2024	0.25	3.6	1.37	ns	ns	n/a
Bromide	mg/L	95	<LOR	5	0.10	ns	ns	n/a
Bromochloroacetic Acid	ug/L	58	<LOR	18	<LOR	ns	ns	n/a
Bromodichloromethane	ug/L	165	<LOR	51	23.8	ns	ns	n/a
Bromoform	ug/L	165	<LOR	32	5.64	ns	ns	n/a
Calcium	mg/L	509	12	48	27.5	ns	ns	n/a
Chlorate	mg/L	58	<LOR	0.42	0.16	ns	ns	n/a
Chlorine (Combined)	mg/L	9105	<LOR	4	1.1	ns	ns	n/a
Chlorine (Free)	mg/L	9102	<LOR	2.6	<LOR	ns	ns	n/a
Chlorodibromomethane	ug/L	165	<LOR	69	20.6	ns	ns	n/a
Chloroform	ug/L	165	10	63	32.5	ns	ns	n/a

Queensland Urban Utilities
SEQ water grid Drinking Water Quality July 2012-June 2013

Colour (True)	PCU	657	180	880	445	ns	ns	n/a
Conductivity	uS/cm	95	n/a	0.31	n/a	ns	ns	n/a
Dibromoacetic Acid	ug/L	58	<LOR	14	<LOR	ns	ns	n/a
Geosmin	ng/L	95	<LOR	8.9	3.1	ns	ns	n/a
Haloacetic Acids (Total)	ug/L	58	<LOR	64	<LOR	ns	ns	n/a
Magnesium	mg/L	509	3.3	32	13.6	ns	ns	n/a
Monobromoacetic Acid	ug/L	58	<LOR	<LOR	<LOR	ns	ns	n/a
Nitrite and Nitrate(as N)	mg/L	1501	0.023	2	0.59	ns	ns	n/a
N-Nitrosodimethylamine	ng/L	12	<LOR	<LOR	<LOR	ns	ns	n/a
Potasium	mg/L	401	1.7	3.5	2.67	ns	ns	n/a
Silica	mg/L	95	5.4	21	12.8	ns	ns	n/a
Sodium	mg/L	401	16	87	41.9	ns	ns	n/a
Temperature	deg C	9082	5	35	24	ns	ns	n/a
Total Organic Carbon	mg/L	94	1.9	4.6	3.06	ns	ns	n/a

Queensland Urban Utilities
SEQ water grid Drinking Water Quality July 2012-June 2013

Definitions

n/a	not applicable
ns	not set

ADWG = Australian Drinking Water Guidelines 2011.
The ADWG 2011 have been developed by the National Health and Medical Research Council (NHMRC) in collaboration with the Natural Resource Management Ministerial Council (NRMMC). The ADWG incorporates the Framework for the Management of Drinking Water Quality and provides the Australian community and the water supply industry with guidance on what constitutes good quality drinking water.

To access the ADWG go to:
http://www.nhmrc.gov.au/_files_nhmrc/publications/attachments/eh52_aust_drinking_water_guidelines_update_120710_0.pdf

Bacteriological quality

Bacteriological quality is assessed by monitoring the water for the organism Escherichia coli as an indicator of contamination. A drinking water scheme is considered bacteriologically safe to drink if no E. coli are found in 98 % of samples analysed.

Chemical parameters

QUU reports yearly on a number of water quality parameters.
The performance for chemical parameters with a health value is assessed as recommended by the ADWG. Performance is deemed as satisfactory if the 95th percentile value is less than the ADWG health guideline value.

Performance for parameters with an aesthetic guideline value is assessed as recommended by the ADWG. Water is considered good quality if the mean value of an aesthetical parameter is measured at less than the recommended maximum criteria described in ADWG.

Figure 6-32. Queensland Urban Utilities SEQ water grid Drinking Water Quality July 2012 – June 2013 report (Queensland Urban Utilities, 2013b).

Table 6-7. The heavy metals that exceeded the ANZECC/ARMCANZ (2000) water quality guidelines for toxicants in the raw waters analysed. Exceedences in each sample are highlighted red. The pH and hardness of each raw water sample is also shown.

Site	Label	pH	Total Hardness	ANZECC/ARMCANZ Trigger values for freshwater 95% level of protection (µg/L)				
				^{27}Al	^{52}Cr	^{63}Cu	^{75}As	^{107}Ag
				55	1.0 (Cr(VI))	1.4	13 (As(V)) 24 (As(III))	0.05
Mt Crosby Westbank WTP	MCR	7.31	87 800	16.5	0.0002	2.44	1.36	1.23
Mt Crosby Westbank WTP	CH1	8.01	94 700	56.4	0.025	1.10	0.888	1.23
Mt Crosby Westbank WTP	CH2	7.99	98 100	66.3	0.083	1.02	0.998	1.23
Brisbane River @ Colleges Crossing	CC	7.37	92 100	7.16	0.035	1.14	1.43	1.23
Oxley Creek	OC	7.22	260 400	0.066	4.87	18.6	23.9	1.28
Wivenhoe Dam	WD	7.26	36 700	726	0.507	1.82	2.41	1.23

Site	Label	pH	Total Hardness	ANZECC/ARMCANZ Trigger values for freshwater 95% level of protection (µg/L)				
				^{27}Al	^{52}Cr	^{63}Cu	^{75}As	^{107}Ag
				55	1.0 (Cr(VI))	1.4	13 (As(V)) 24 (As(III))	0.05
Lake Somerset - "The Spit"	**LS**	7.54	23 800	214	0.275	1.48	2.34	1.23
Baroon Pocket Lake and Dam	**BP**	7.21	12 000	28.2	0.028	0.477	0.358	1.23
Ewan Maddock Dam	**EM**	6.59	4105	65.8	0.067	0.217	0.879	1.23
Ewan Maddock Dam	**EM2**	5.63	4470	51.2	0.102	0.174	0.875	1.23
Lake Samsonvale - Forgan Cove	**LS FC**	6.93	17 300	95.0	0.202	0.907	1.53	1.23
Lake Samsonvale - Bullockys Rest	**LS BR**	7.43	15 800	240.8	0.517	1.22	1.43	1.24

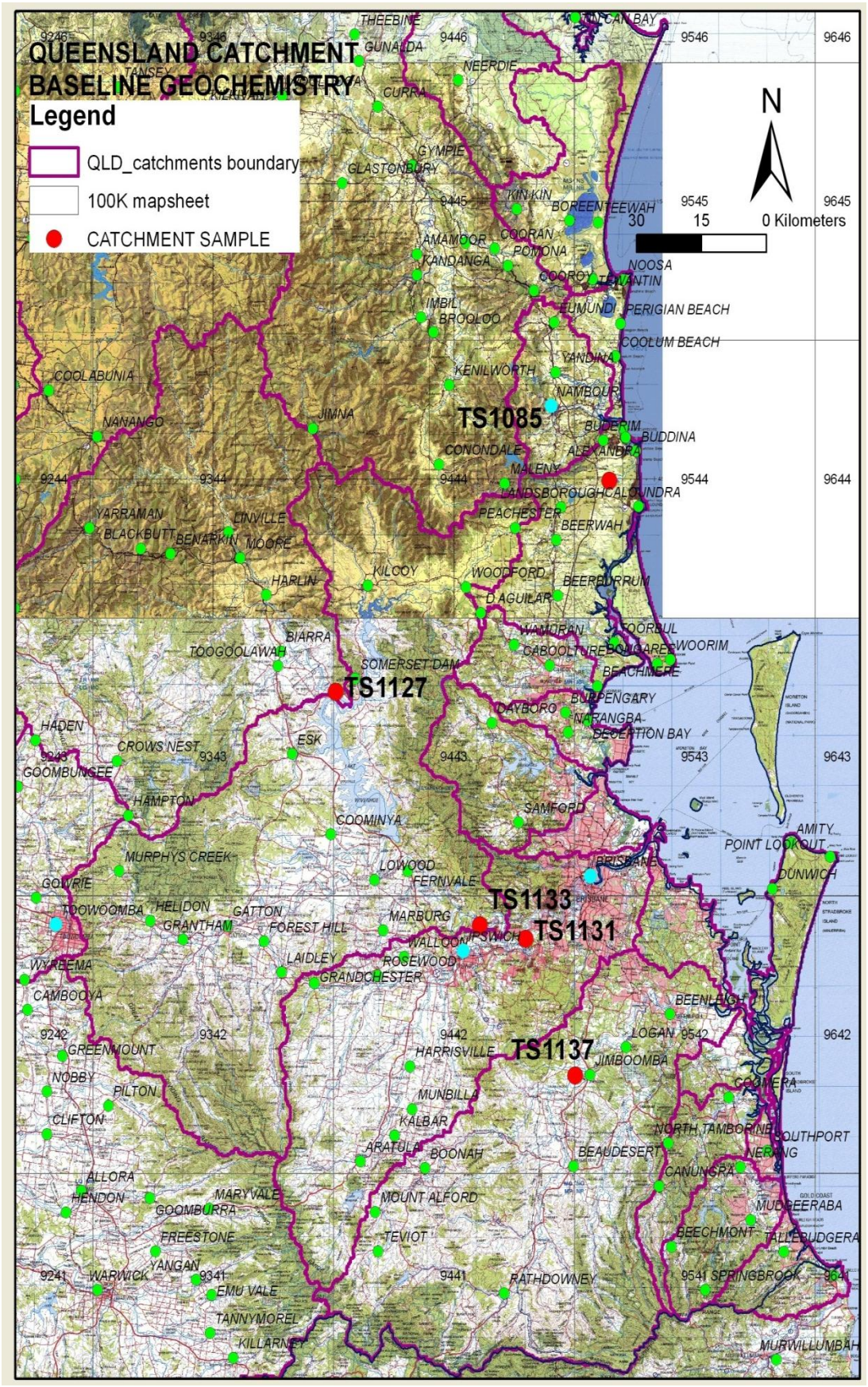


Figure 6-33. Map of SEQ Catchment Samples from Queensland's Mineral Prospectivity Atlas (Tang & Brown, 2011). Relevant sample sites: TS1085 - Mary River; TS1133 – Brisbane River at College's Crossing; TS1127 - Brisbane River between Lake Somerset and Lake Wivenhoe.

C-4 Partial Least Squares Analysis

Table 6-8. The R^2 and Q^2 values for the randomly permuted data, and the R^2 and Q^2 values of the original model.

Y Variables	R^2	Q^2
ORIGINAL	**0.657**	**0.44**
Be / 9 [#1]	0.0939	-0.364
Be / 9 [#2]	0.111	-0.379
Be / 9 [#3]	0.107	-0.309
K / 39 [#1]	0.0855	-0.256
K / 39 [#2]	0.119	-0.704
K / 39 [#3]	0.101	-0.498
Fe / 57 [#1]	0.112	-0.274
Fe / 57 [#2]	0.111	-0.338
Fe / 57 [#3]	0.0933	-0.149
As / 75 [#1]	0.111	-0.245
As / 75 [#2]	0.126	-0.311
As / 75 [#3]	0.123	-0.712
Se / 78 [#1]	0.125	-0.829
Se / 78 [#2]	0.125	-0.781
Se / 78 [#3]	0.105	-0.701
Cd / 111 [#1]	0.115	-0.449
Cd / 111 [#2]	0.126	-0.489
Cd / 111 [#3]	0.116	-0.44
Sb / 121 [#2]	0.124	-0.766
Sb / 121 [#3]	0.116	-0.588
Ba / 137 [#1]	0.108	-0.628
Ba / 137 [#2]	0.124	-0.653
Ba / 137 [#3]	0.109	-0.477
Hg / 202 [#3]	0.102	-0.121
Th / 232 [#1]	0.127	-0.419
Th / 232 [#2]	0.107	-0.313
Th / 232 [#3]	0.0965	-0.151

Table 6-9. The R^2 and RMSEP values for every tuning step and element in the Y variable block.

Y Variables	R^2	RMSEP
Be / 9 [#1]	1	0.0665606
Be / 9 [#2]	0.2086	0.0778623
Be / 9 [#3]	1	0.0869719
K / 39 [#1]	0.4323	9346.29
K / 39 [#2]	0.09713	1535.6
K / 39 [#3]	0.3625	1361.94
Fe / 57 [#1]	0.5107	212.513
Fe / 57 [#2]	0.02008	312.245
Fe / 57 [#3]	0.00417	3016.51
As / 75 [#1]	0.03292	0.595732
As / 75 [#2]	0.05097	0.656397
As / 75 [#3]	0.00117	0.473048
Se / 78 [#1]	0.06288	0.931637
Se / 78 [#2]	0.145	2.06297
Se / 78 [#3]	0.1944	0.86268
Cd / 111 [#1]	0.1573	0.587038
Cd / 111 [#2]	0.1506	0.596637
Cd / 111 [#3]	0.116	0.600573
Sb / 121 [#2]	1	0.0379463
Sb / 121 [#3]	0.1472	0.240147
Ba / 137 [#1]	(-)1	8.32963
Ba / 137 [#2]	(-)1	7.99955
Ba / 137 [#3]	0.07609	16.1005
Hg / 202 [#3]	0.04676	1511.49
Th / 232 [#1]	(-)1	0.00814343
Th / 232 [#2]	1	0.00781003
Th / 232 [#3]	0.001832	0.207258

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